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(54) Title: LIQUID CRYSTAL COMPOUNDS HAVING A CHIRAL FLUORINATED TERMINAL PORTION

(57) Abstract

Fluorine-containing, chiral liquid crystal compounds comprise (a) a chiral fluorochemical terminal portion comprising (i) at least one chiral center, which can optionally be heteroatom-substituted; (ii) a terminal fluoroalkyl, fluoroether, perfluoroalkyl, or perfluoroether group; and (iii) an alkylene or fluoroalkylene group optionally containing at least one catenary ether oxygen atom; (b) a chiral or achiral terminal portion consisting of a hydrocarbon or hydrocarbon ether group, and, when chiral, comprising at least one chiral center, which can optionally be heteroatom-substituted; and (c) a central core connecting the terminal portions; the alkylene or fluoroalkylene group of the chiral fluorochemical terminal portion having at least 3 in-chain atoms and being located between the chiral center of the chiral fluorochemical terminal portion and the central core. The compounds have smectic mesophases or latent smectic mesophases and are useful, for example, in liquid crystal display devices.

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LIQUID CRYSTAL COMPOUNDS HAVING A CHIRAL FLUORINATED TERMINAL PORTION

Field of the Invention

This invention relates to fluorinated chiral smectic liquid crystal compounds, to a process for the preparation of such compounds (and to intermediates for use therein), and to liquid crystal compound mixtures and electrooptical display devices containing such compounds.

Background of the Invention

Devices employing liquid crystals have found use in a variety of electrooptical applications, in particular those which require compact, energy-efficient, voltage-controlled light valves, e.g., watch and calculator displays, as well as the flat-panel displays found in portable computers and compact televisions. Liquid crystal displays have a number of unique characteristics, including low voltage and low power of operation, which make them the most promising of the non-emissive electrooptical display candidates currently available.

One of the most important characteristics of a liquid crystal display device is its response time, i.e., the time required for the device to switch from the on (light) state to the off (dark) state. In a ferroelectric or anti-ferroelectric device, response time ($\tau=\eta/P_sE$) is proportional to the rotational viscosity (η) of the liquid crystal compound(s) contained within the device and is inversely proportional to their polarization (P_s) and to the applied electric field (E). Thus, response time can be reduced by using compound(s) having high polarizations

or low viscosities, and such compounds are greatly desired in the art.

In the passive addressing of liquid crystal compounds exhibiting a spontaneous polarization, however, low polarization mixtures can be important for the practical operation of a liquid crystal device. Polarization reversal fields are larger for higher polarization mixtures, and polarization reversal fields cause switching or partial switching back to a material's original director alignment. This results in loss of the bistability that is crucial to the passive-matrix driving of ferroelectric liquid crystal devices.

Another potential disadvantage of using high polarization mixtures is the partial switching of their director alignment in response to non-switching (secondary) signals in a driving waveform. This continued response or fluctuation of the director causes a large decrease in the contrast ratio of a ferroelectric liquid crystal device.

In addition to fast response times, compounds should ideally possess broad smectic temperature ranges to enable operation of the device over a broad range of temperatures (or should be capable of combination with other liquid crystal compounds having different smectic temperature ranges without adversely affecting the smectic phase behavior of the base mixture).

Summary of the Invention

Briefly, in one aspect, this invention provides fluorine-containing, chiral liquid crystal compounds having smectic mesophases or latent smectic mesophases. (Compounds having latent smectic mesophases are those which by themselves do not exhibit a smectic mesophase, but which, when in admixture with compounds having

smectic mesophases or with other compounds having latent smectic mesophases, develop smectic mesophases under appropriate conditions.) The chiral liquid crystal compounds of the invention comprise (a) a chiral fluorochemical terminal portion that comprises (i) at least one chiral center (or chiral moiety), which can optionally be heteroatom-substituted; (ii) a terminal fluoroalkyl, fluoroether, perfluoroalkyl, or perfluoroether group (preferably, perfluoroalkyl or perfluoroether); and (iii) an alkylene or fluoroalkylene group optionally containing at least one catenary, i.e., in-chain, ether oxygen atom; (b) a chiral or achiral terminal portion consisting of a hydrocarbon or hydrocarbon ether group and, when chiral, comprising at least one chiral center, which can optionally be heteroatom-substituted; and (c) a central core connecting the terminal portions; the alkylene or fluoroalkylene group of the chiral fluorochemical terminal portion having at least 3 in-chain atoms and being located between the chiral center of the chiral fluorochemical terminal portion and the central core (an "extended group").

The chiral fluorochemical terminal portion of the compounds of the invention can be represented by the formula $-D-R^*-D-R_f$, where R^* is a cyclic or acyclic chiral moiety containing at least one chiral center (asymmetric carbon atom); R_f is fluoroalkyl, perfluoroalkyl, fluoroether, or perfluoroether; and each D is independently and non-directionally selected from the group consisting of

a covalent bond,

$-C(=O)-O-C_rH_{2r}-$, $-O-C_rH_{2r}-$, $-O-(O=)C-C_rH_{2r}-$, $-C\equiv C-$, $-CH=CH-$, $-C(=O)-$,

$-O\!\left(C_sH_{2s}O\right)_{t}C_{r'}H_{2r'}-$, $-C_rH_{2r}-$, $\left(C_sH_{2s}O\right)_{t}C_{r'}H_{2r'}-$, $-O-$, $-S-$,

$-OSO_2-$, $-SO_2-$, $-SO_2-C_rH_{2r}-$, $\underset{\displaystyle C_pH_{2p+1}}{-C_rH_{2r}-\underset{|}{N}-SO_2-}$, $-N(C_pH_{2p+1})-$,

$-C_rH_{2r}-N-C(=O)-$, $-CH=N-$,

and combinations thereof, where one or more hydrogen atoms can optionally be replaced with fluorine, and where r and r' are independently integers of 0 to about 20, s is independently an integer of 1 to about 10 for each $(C_sH_{2s}O)$, t is an integer of 1 to about 6, and p is an integer of 0 to about 4; with the proviso that at least one chiral center of R* is spaced from the central core by at least 3 in-chain atoms. Preferably, R_f is perfluoroalkyl or perfluoroether; more preferably, R_f is perfluoroether, as the perfluoroether-containing compounds of the invention exhibit, e.g., a broad smectic C mesophase, good compatibility with other smectic C compounds, and advantageous layer spacing behavior. When the R_f group of the fluorochemical terminal portion is perfluoroalkyl or perfluoroether, it can contain small amounts of residual carbon-bonded hydrogen atoms but is preferably completely fluorinated.

In general, the compounds of this invention have a central core comprised of at least one or two rings independently selected from the group consisting of aromatic, heteroaromatic, alicyclic, substituted aromatic, substituted heteroaromatic, and substituted alicyclic rings, the rings being connected one with another by a covalent bond or by chemical groups selected from the group consisting of -COO-, -COS-, -HC=N-, -CH=CH-, -C≡C-, and -COSe-. The rings can be fused or non-fused. The heteroatoms within the heteroaromatic rings comprise at least one atom selected from the group consisting of nitrogen, oxygen,

and sulfur. Non-adjacent ring carbon atoms in the alicyclic rings can be substituted by nitrogen, oxygen, or sulfur atoms. When the ring(s) are aromatic, heteroaromatic, substituted aromatic, or substituted heteroaromatic, the non-fused rings of the core are preferably no more than about two in number.

The chiral liquid crystal compounds of the invention exhibit exceptionally wide mesomorphic temperature ranges. When used in electrooptical devices, the compounds provide fast response times upon application of an electric field over broad temperature ranges. This makes them extremely useful in the preparation of mixtures that operate in their active mesomorphic phase in the range of from about -30°C to about 70°C.

Surprisingly, in comparison with similar compounds having fewer than 3 in-chain atoms between at least one chiral center of the fluorochemical terminal portion and the central core, the compounds of the invention provide comparable electrooptic response speeds in spite of their lower measured polarization values. These lower polarization values in combination with broad mesogenic temperature ranges enable the utilization of liquid crystal mixtures that contain up to 100% of the chiral (optically active) compounds of the invention. In general, mixtures containing a high concentration of the compounds of this invention exhibit more temperature independent switching properties, which is important for the reliable and consistent operation of liquid crystal devices.

Furthermore, the use of high concentrations of liquid crystal compounds having low polarizations also provides a decrease (relative to the use of low concentrations of compounds having high polarizations) in the partial switching response of the resulting

compositions to non-switching (secondary) signals in the driving waveform that is commonly used in the passive addressing of liquid crystal devices. Such a decrease in this response is critical for improving the contrast of a device.

The compounds of the invention are useful in admixture with themselves or with other chiral or achiral liquid crystal compounds (as dopants or as the major components), for electrooptical display applications. The compounds have a number of desirable properties when used in admixture with themselves or with other liquid crystal compounds, preferably compounds having fluorinated terminal portions such as those compounds disclosed, for example, in U.S. Pat. Nos. 4,886,619 (Janulis), 5,082,587 (Janulis), 5,262,082 (Janulis et al.), and 5,658,491 (Kistner et al.).

For example, the compounds of the invention when admixed with such preferred liquid crystal compounds show excellent compatibility, show a beneficial effect or only a minimal negative effect on the smectic C temperature range of the resulting mixtures (even when present at high concentrations), and provide ferroelectric mixtures having fast electrical response times. Mixtures containing the compounds exhibit favorable alignment, switching, response to an electric field, temperature dependence of response speed, temperature dependence of polarization, contrast, layer structure, and mesomorphic temperature ranges. Compounds of the invention can also be used to optimize mixture properties such as tilt angle, memory angle, spontaneous polarization and its temperature dependence, mesomorphic transition temperatures, switching behavior, birefringence, and the temperature dependence of layer spacing.

In other aspects, this invention also provides liquid crystal compounds (described below) having two fluorochemical terminal portions, a mixture of liquid crystal compounds comprising at least one liquid crystal compound of the invention, a liquid crystal display device containing at least one liquid crystal compound of the invention, and liquid crystal intermediate compounds.

Brief Description of the Drawing

These and other features, aspects, and advantages of the present invention will become better understood with regard to the following description, appended claims, and accompanying drawing, wherein:

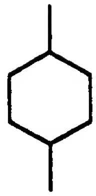
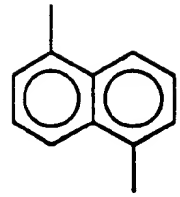
Figure 1 shows a plot of smectic C layer spacing (in Angstroms) versus temperature (in degrees Centigrade) for selected compounds of the invention that were prepared by the procedures given in the designated Examples.

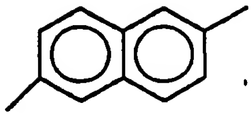
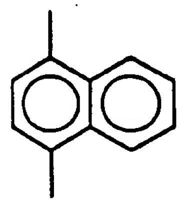
Detailed Description of the Invention

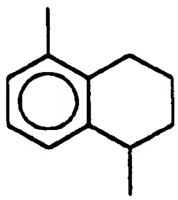
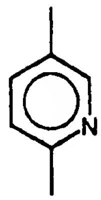
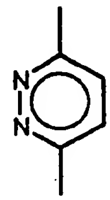
A class of the above-described liquid crystal compounds of the present invention can be represented by the general formula I:

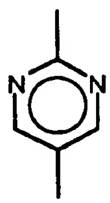
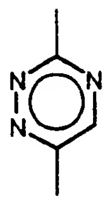
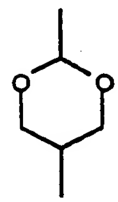
$$R-\underset{\substack{|\\X_l}}{(M)_a}-A\underset{\substack{|\\Y_m}}{(N)_b}B\underset{\substack{|\\Z_n}}{(P)_c}-D-R^*-D-R_f \qquad (I)$$

where M, N, and P are each independently selected from the group consisting of

 ,  ,  ,

 ,  ,

 ,  ,  ,

 ,  , and 

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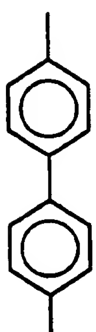
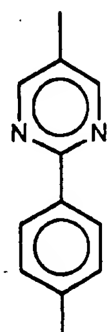
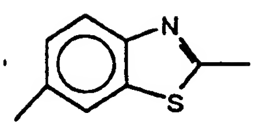
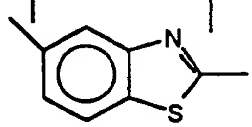
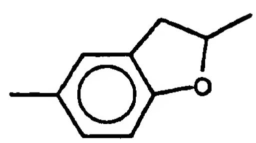
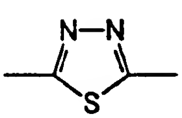
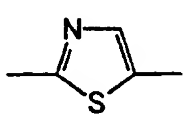
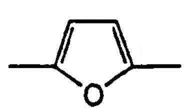
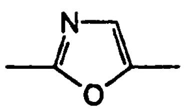
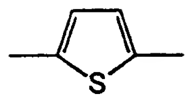
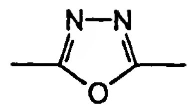
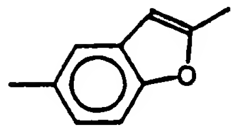
 ,  ,  ,

 and 

 ,  ,  ,

, , , and



a, b, and c are each independently zero or an integer of from 1 to 3, with the proviso that the sum of a + b + c be at least 1 (and preferably no greater than 2);

each A and B are non-directionally and independently selected from the group consisting of a covalent bond,

-C(=O)-O-, -C(=O)-S-, -C(=O)-Se-,

-C(=O)-Te-, $-(CH_2CH_2)_k-$ where k is 1 to 4, -CH=CH-, -C≡C-, -CH=N-, $-CH_2-O-$, -C(=O)-, and -O- ;

each X, Y, and Z are independently selected from the group consisting of -H, -Cl, -F, -Br, -I, -OH, $-OCH_3$, $-CH_3$, $-CF_3$, $-OCF_3$, -CN, and $-NO_2$;

each l, m, and n are independently zero or an integer of 1 to 4;

each D is non-directionally and independently selected from the group consisting of a covalent bond, $-C(=O)-O-C_rH_{2r}-$, $-O-C_rH_{2r}-$, $-O-(O=)C-C_rH_{2r}-$, -C≡C-, -CH=CH-, -C(=O)-,

$-O(C_sH_{2s}O)_tC_{r'}H_{2r'}-$, $-C_rH_{2r}-$, $(C_sH_{2s}O)_tC_{r'}H_{2r'}-$, $-O-$, $-S-$,

$-OSO_2-$, $-SO_2-$, $-SO_2-C_rH_{2r}-$, $-C_rH_{2r}-N(C_pH_{2p+1})-SO_2-$, $-N(C_pH_{2p+1})-$,

$-C_rH_{2r}-N(C_pH_{2p+1})-C(=O)-$, $-CH=N-$, and combinations thereof,

where one or more hydrogen atoms can optionally be replaced with fluorine, and where r and r' are independently integers of 0 to about 20, s is independently an integer of 1 to about 10 for each $(C_sH_{2s}O)$, t is an integer of 1 to about 6, and p is an integer of 0 to about 4;

R is selected from the group consisting of

$-O-((C_{q'}H_{2q'-v'}-(R')_{v'})-O)_w-C_qH_{2q+1-v}-(R')_v$,

$-((C_{q'}H_{2q'-v'}-(R')_{v'})-O)_w-C_qH_{2q+1-v}-(R')_v$,

$-C(=O)-O-C_qH_{2q+1-v}-(R')_v$, $-O-(O=)C-C_qH_{2q+1-v}-(R')_v$,

```
      D
     / \
  —W   W—CqH2q+1-v—(R')v , and
     \ /
      D
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$-CR'H-(D)_g-CR'H-C_qH_{2q+1-v}-(R')_v$,

where each R' is independently selected from the group consisting of -Cl, -F, $-CF_3$, $-NO_2$, -CN, -H, $-C_qH_{2q+1}$, $-O-(O=)C-C_qH_{2q+1}$, $-C(=O)-O-C_qH_{2q+1}$, -Br, -OH, and $-OC_qH_{2q+1}$ (preferably, -H or -F); q' is independently an integer of 1 to about 20 for each $(C_{q'}H_{2q'}-O)$; q is an integer of 1 to about 20; w is an integer of 0 to about 10; v is

an integer of 0 to about 2; each v' is independently an integer of 0 to about 2; g is an integer of 1 to about 3; each D is independently and non-directionally selected from the group set forth for D above, with the proviso that the ring containing D has from about 3 to about 10 ring atoms; each W is independently selected from the group consisting of N, CR′, and SiR′; and R can be chiral or achiral; and

R* is a cyclic or acyclic chiral moiety containing at least one chiral center; and

R_f is fluoroalkyl, perfluoroalkyl, fluoroether, or perfluoroether;

with the proviso that there are at least 3 in-chain atoms between the central core structure $-(M)_a-A-(N)_b-B-(P)_c-$ and at least one chiral center of R*.

Preferably, R_f is perfluoroalkyl or perfluoroether and R* is selected from the group consisting of

$-O-((C_{q'}H_{2q'-v'}-(R')_{v'})-O)_w-C_qH_{2q-v}-(R')_v-$,

$-((C_{q'}H_{2q'-v'}-(R')_{v'})-O)_w-C_qH_{2q-v}-(R')_v-$,

$-C(=O)-O-C_qH_{2q-v}-(R')_v-$, $-O-(O=)C-C_qH_{2q-v}-(R')_v-$,

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        D
       / \
  ——W     W——, and -CR'H-(D)g-CR'H- ,
       \ /
        D
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where each R' is independently selected from the group consisting of -Cl, -F, $-CF_3$, $-NO_2$, -CN, -H, $-C_qH_{2q+1}$,

$-O-(O=)C-C_qH_{2q+1}$, $-C(=O)-O-C_qH_{2q+1}$, -Br, -OH, and $-OC_qH_{2q+1}$ (preferably, -H, -F, $-CF_3$, -Br, -OH, or $-OCH_3$; more preferably, -H, -F, or $-CF_3$); q' is independently an integer of 1 to about 20 for each $((C_{q'}H_{2q'-v'}-(R')_{v'})-O)$; q is an integer of 1 to about 20; w is an integer of 0 to about 10; v is an integer of 0 to about 3; each v' is independently an integer of 0 to about 3; g is an integer of 1 to about 3; each D is independently and non-directionally selected from the group set forth for D above, with the proviso that the ring containing D has from about 3 to about 10 ring atoms; and each W is independently selected from the group consisting of N, CR', and SiR'. More preferably, R_f is perfluoroether.

In defining R_f, particularly preferred perfluoroalkyl groups are those which can be represented by the formula $-C_qF_{2q}X'$, where q is as defined above (and, preferably, is at least about 5) and X' is hydrogen or fluorine. Particularly preferred perfluoroether groups are those which can be represented by the formula $-(C_xF_{2x}O)_zC_yF_{2y+1}$, where x is independently an integer of 1 to about 10 for each $(C_xF_{2x}O)$, y is an integer of 1 to about 10, and z is an integer of 1 to about 10. Preferably, the perfluoroether group is linear, x is independently an integer of 1 to about 6 for each $(C_xF_{2x}O)$, y is an integer of 1 to about 6, and z is an integer of 1 to about 6.

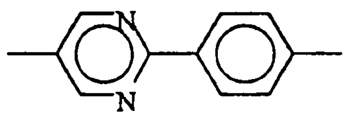
Preferred subclasses of the above-described chiral compounds of the invention can be represented by the following formula:

$$R''-(O)_j-G-D'-R^*-(C_{s'}H_{2s'}O)_{t'}C_{r''}H_{2r''}-R_f \quad \text{(II)}$$

where R'' is $(R')_v-C_qH_{2q+1-v}$, where q is an integer of 2 to about 10, each R' is independently selected from the group consisting of hydrogen, fluorine, chlorine, methyl, and perfluoromethyl, and v is an integer of 1 to about 2;

j is an integer of 0 or 1;

G is selected from the group consisting of



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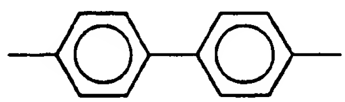

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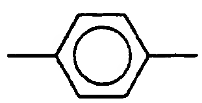

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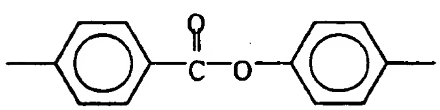


,

where one or more of the aromatic hydrogen atoms can be replaced with fluorine;

D' is selected from the group consisting of $-O-(C_sH_{2s}O)_t-C_{r'}H_{2r'}-$, $-C_rH_{2r}-$, $-(C_sH_{2s}O)_t-C_{r'}H_{2r'}-$, and $-O-C_rH_{2r}-$, where r and r' are independently integers of 0 to about 12, s is independently an integer of 1 to about 10 for each $(C_sH_{2s}O)$, and t is an integer of 1 to about 3;

R* is selected from the group consisting of

$-C_qH_{2q-v}-(R')_v-$ and

```
      D"
     / \
 —W     W—,
     \ /
      D"
```

where R′ is -F, q is an integer of 1 to about 4, v is an integer of 1 to about 3, W is N or CH, and D″ is $-C(=O)-O-$ or $-CH_2-$;

s′ in Formula II is an integer of 1 to about 6;

t′ in Formula II is an integer of 0 or 1;

r″ in Formula II is an integer of 1 to about 3; and

R_f is selected from the group consisting of $-C_qF_{2q+1}$ and $-(C_xF_{2x}O)_zC_yF_{2y+1}$, where q is an integer of 1 to about 6, x is independently an integer of 1 to about 10 for each $(C_xF_{2x}O)$, y is an integer of 1 to about 8, and z is an integer of 1 to about 5;

with the proviso that there are at least 3 in-chain atoms between the central core structure G and at least one chiral center of R*.

More preferably, s′, t′, and r″ in Formula II are each an integer of 1.

The fluorine-containing liquid crystal compounds of the invention can be prepared by a process comprising the steps of (a) mixing at least one compound represented by the formula

$$R\underset{\substack{|\\X_l}}{(M)}_a A\underset{\substack{|\\Y_m}}{(N)}_b\text{-}D\text{-}(R^*)_x\text{-}B' \qquad \text{(III)}$$

with at least one compound represented by the formula

$$B''\underset{\substack{|\\Z_n}}{(P)}_c\text{-}D\text{-}R^*\text{-}D\text{-}R_f \qquad \text{(IV)}$$

or mixing at least one compound represented by the formula

$$R\underset{\substack{|\\X_l}}{(M)}_a\text{-}D\text{-}(R^*)_x\text{-}A' \qquad \text{(V)}$$

with at least one compound represented by the formula

$$A''\underset{\substack{|\\Y_m}}{(N)}_b B\underset{\substack{|\\Z_n}}{(P)}_c\text{-}D\text{-}R^*\text{-}D\text{-}R_f \qquad \text{(VI)}$$

or mixing at least one compound represented by the formula

$$R\underset{\substack{|\\X_l}}{(M)}_a A\underset{\substack{|\\Y_m}}{(N)}_b\text{-}D\text{-}(R^*)_x\text{-}B' \qquad \text{(III)}$$

with at least one compound represented by the formula

$$B''\text{-}D\text{-}R_f \qquad \text{(VII)},$$

where M, N, P, a, b, c, A, B, X, Y, Z, l, m, n, D, R, R^*, and R_f are as defined above for formula I; x is an integer of 0 or 1; and each A', A'', B', and B'' are

independently selected from the group consisting of -H, -Cl, -Br, -I, -OH, -COOH, $-CH(CH_2OH)_2$, -SH, -SeH, -TeH, $-NH_2$, -COCl, -CHO, $-OSO_2R_f'''$, $-OSO_2CH_3$, $-C\equiv CH$, dialkyl borane, $-CH=CH_2$, $-NH(C=O)OC_qH_{2q+1}$, -NCO, $-OSO_2-cyclo(C_6H_4)-CH_3$, $-CH_2COOH$, and $-CH(C(O)O-C_qH_{2q+1})_2$, where R_f''' is a perfluoroalkyl group having from 1 to about 10 carbon atoms and q is an integer of 0 to about 20, and with the proviso that $(R^*)_x-A'$ can enter into an addition or condensation reaction with A'' and that $(R^*)_x-B'$ can enter into an addition or condensation reaction with B'';

and (b) allowing compounds III and IV, compounds V and VI, or compounds III and VII to react, optionally in the presence of suitable coupling agent(s), i.e., reagent(s) which effect coupling. For Formula IV, B'' is preferably selected from the group consisting of $-C\equiv CH$, dialkyl borane, and $-CH=CH_2$ (more preferably $-CH=CH_2$), and $-D-R^*-D-R_f$ is preferably $-D'-R^*-(C_{s'}H_{2s'}O)_{t'}C_{r''}H_{2r''}-R_f$ as defined above for Formula II.

In another aspect, liquid crystal compounds of the present invention also include compounds that have two fluorochemical terminal portions and can be represented by the general formula VIII:

$$R_f-CH_2O-C_{n'}H_{2n'}-(O)_j-(M)_a-\underset{\substack{|\\X_1}}{A}-(\underset{\substack{|\\Y_m}}{N})_b-B-(\underset{\substack{|\\Z_n}}{P})_c-D-R^*-D-R_f \qquad \text{(VIII)}$$

where n' is an integer of 0 to about 10 (preferably from about 2 to about 6); j is an integer of 0 or 1; each R_f moiety is independently selected from the group consisting of fluoroalkyl, fluoroether, perfluoroalkyl, and perfluoroether (preferably, perfluoroalkyl or

perfluoroether; more preferably, perfluoroether); and definitions (and preferred definitions) for the other moieties are as stated above for Formula I. Such compounds can be prepared by the above-described methods involving Formulas III, IV, V, VI, and VII, wherein the R moiety is replaced with R_f-CH_2O-$C_{n'}H_{2n'}O$- (wherein R_f and n′ are as defined for Formula VIII).

Preferred subclasses of the above-described chiral compounds of the invention having two fluorochemical terminal portions can be represented by the following formula:

$$R_f\text{-}CH_2O\text{-}C_{n'}H_{2n'}O\text{-}G\text{-}D'\text{-}R^*\text{-}(C_{s'}H_{2s'}O)_{t'}C_{r''}H_{2r''}\text{-}R_f \qquad \text{(IX)}$$

where n′ is an integer of about 2 to about 6 (preferably, 3 or 4); each R_f is independently selected from the group defined above for R_f in regard to Formula II; and all other moieties (and preferred moieties) are as defined above for Formula II.

Most of the compounds of the present invention have enhanced smectic mesophases. Mixtures of the compounds of the invention with other liquid crystal materials can be formulated to provide desired transition temperatures and broad mesophase temperature ranges. Such mixtures preferably contain compounds having fluorinated terminal portions, such as those compounds described, for example, in U.S. Pat. Nos. 4,886,619 (Janulis) and 5,082,587 (Janulis) and, most preferably, 5,262,082 (Janulis et al.) and 5,658,491 (Kistner et al.). The liquid crystal compounds of the invention can also be used to prepare ferroelectric liquid crystal devices such as, e.g., those described in U.S. Patent Nos. 5,417,883 (Radcliffe) and 5,641,427 (Shinjo) and in EP 769582 and EP 769543.

The compounds of this invention in admixture with other chiral or achiral liquid crystal compounds may exhibit chiral smectic liquid crystal behavior. Furthermore, many of the perfluoroether group-containing liquid crystal compounds of the invention when used alone or when mixed with other liquid crystal compounds of the invention or with achiral, fluorine-containing liquid crystal compounds (preferably, the perfluoroether group-containing liquid crystal compounds described in U.S. Pat. No. 5,262,082 (Janulis et al.)) exhibit a reduced temperature dependence of the smectic interlayer spacing. This property provides for the spontaneous generation of an essentially bookshelf type layer structure, which is ideal for a ferroelectric liquid crystal device. In general, the compounds of the invention exhibit maintenance or expansion of the smectic C layer spacing with decreasing temperature.

Another advantage of using the materials of this invention in the formulation of liquid crystal mixtures is the low birefringence which can be obtained. The low birefringence of the liquid crystal compounds of the invention (relative to their non-fluorine-containing analoques) allows the fabrication of devices with larger device spacings. Light transmission through, e.g., a surface-stabilized ferroelectric device (as described in U.S. Patent No. 4,367,924) with two polarizers is represented by the following equation:

$$I = I_o\ (\sin^2(4\Theta))\ (\sin^2(\pi\Delta nd/\lambda))$$

where I_o = transmission through parallel polarizers

Θ = material tilt angle

Δn = liquid crystal birefringence

d = device spacing

λ = wavelength of light used

To maximize the transmission, both $\sin^2(4\Theta)$ and $\sin^2(\pi\Delta nd/\lambda)$ must be at maximum. This occurs when each term equals one. The first term is a maximum when the tilt angle equals 22.5°. This is a function of the liquid crystal and is constant for a given material at a given temperature. The second term is maximum when $\Delta nd = \lambda/2$. This demonstrates the criticality of the low birefringence of the materials of this invention. Low birefringence allows a larger device thickness, d, for a given wavelength of light. Thus, a larger device spacing is possible while still maximizing transmission, allowing easier device construction.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

In the following examples, all temperatures are in degrees Celsius and all parts and percentages are by weight unless indicated otherwise. Commercially available materials were chemically transformed by reaction pathways well-known to those skilled in the art and detailed in the examples. Chemical transformations were comprised of acylation, esterification, etherification, alkylation, and combinations thereof using fluorine-containing and non-fluorine-containing reactants to provide the precursor compounds, which, in turn, were caused to react

together to yield the chiral, fluorine-containing liquid crystal compounds of this invention.

Compounds prepared in the various examples of this invention were characterized by their melting or boiling point, and structures were confirmed by using at least one of the following methods of analysis: chromatography; ^{13}C-, ^{1}H-, and ^{19}F-NMR; and infrared and mass spectroscopies.

EXAMPLES

The 5-alkyl-2-(4-hydroxyphenyl) pyrimidines used in the examples were prepared essentially as described by Zaschke and Stolle in "Synthese niedrigschmelzender Kristallin-Flussiger Heterocyclen; 5-n-Alkyl-2-[4-n-alkanoyloxy-phenyl]pyrimidine," Z.Chem. 15, 441-3 (1975). (S)- and (R)-2-fluoro-decyl-p-toluenesulfonate were prepared essentially as described by Nohira et al. in Mol. Cryst. Liq. Cryst. 180B, 379 (1990). Fluorinated alcohols were prepared essentially as described in U.S. Patent No. 5,262,082 (Janulis et al.) by sodium borohydride reduction of the corresponding perfluorinated acids (or derivatives), which had been prepared by electrochemical fluorination (ECF) or by direct fluorination (using elemental fluorine) of the corresponding hydrocarbon acids (or derivatives). See, e.g., the description of ECF given in U.S. Patent No. 2,519,983 (Simons). Direct fluorination is described, e.g., in U.S. Patent No. 5,362,919 (Costello et al.).

Example 1

Preparation of (S)-5-Octyl-2-[4-(8-(2-(2-(2-(trifluoromethoxy(tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-7-fluorooctyl)phenyl]pyrimidine

Preparation of Starting Material:
(S)-8-(2-(2-(2-(Trifluoromethoxy(tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-7-fluorooct-1-ene

Into a dry 3 liter flask fitted with a reflux condenser, a nitrogen inlet, a thermocouple, and an addition funnel, were placed magnesium turnings (37.8 g, 1.55 mol) and dry t-butylmethylether (100 mL). 5-bromo-1-pentene (225 g, 1.51 mol) was added to the flask dropwise at a rate which maintained the reflux temperature of the reaction mixture (55-6°C). Additional t-butylmethylether (about 1.5 L) was added in 50 mL portions during the addition of the bromide. After the addition was complete, the resulting mixture was heated to reflux for an additional 30 minutes. The mixture was then cooled to -65°C. Dilithiotetrachlorocuprate (302 mL, 0.1 M in tetrahydrofuran (THF)) was added, and the resulting reaction mixture was stirred for 45 minutes at -65°C followed by addition of R(-)-epichlorohydrin (125.7 g, 1.36 mol) at a rate not to exceed a reaction mixture temperature of -40°C. The reaction mixture was stirred for an additional 30 minutes, was warmed to -5°C, and was then quenched by the addition of 250 g of ammonium chloride in 2.5 liters of water. The resulting aqueous phase was extracted with t-butylmethylether (300 mL), and the combined ether layers were washed with ammonium chloride/ammonium hydroxide buffer (2x500 mL) and saturated sodium chloride (2x500 mL). The solvent was removed under reduced pressure, and the resulting residue was distilled (b.p. = 57 - 72°C at 0.15 torr) to give 183 g of (R)-8-chloro-7-hydroxy-oct-1-ene.

This chlorohydrin was converted in situ to (R)-1,2-epoxy-7-octene and reacted with 2-(2-(2-

(trifluoromethoxy(tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethanol using the following procedure: (R)-8-chloro-7-hydroxy-oct-1-ene (100 g, 0.61 mol), aqueous potassium hydroxide (45 mL of 45 wt.%), 2-(2-(2-(trifluoromethoxy(tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethanol (291 g, 0.733 mol), Adogen™ 464 (60 g), and 1,2-dimethoxyethane (60 mL) were added to a one liter flask fitted with a mechanical stirrer, an addition funnel, a reflux condenser, and a thermometer. The resulting solution was stirred for one hour at 45°C and then warmed to 60°C, at which time aqueous potassium hydroxide (70 mL of 45 wt%) was added dropwise. This solution was heated for 2 hours at 60°C and then at 70°C for 8 hours. Water (300 mL) was added, and the resulting organic phase was separated and washed with 7 weight % HCl (300 mL). The organic phase was again separated and was concentrated under reduced pressure (25 torr). The resulting crude product was then purified by silica gel chromatography using toluene as eluent to give 268 g of (R)-8-(2-(2-(2-(trifluoromethoxy(tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-7-hydroxyoct-1-ene.

Under a nitrogen atmosphere, (R)-8-(2-(2-(2-(trifluoromethoxy(tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-7-hydroxyoct-1-ene (60 g, 0.103 mol) and dry toluene (120 mL) were added to an oven-dried flask with stirring. The resulting solution was cooled to -15°C, perfluorobutanesulfonyl fluoride (58.9 g, 0.185 mol) was added, and the resulting reaction mixture was stirred for 5 minutes. 1,8-Diazabicyclo[5.4.0]undec-7-ene (28.7 g, 0.189 mol) was then added at a rate so as not to exceed a temperature of 5°C for the reaction mixture. The reaction mixture

was stirred for 1 hour at ambient temperature and was quenched by the addition of toluene (120 mL) and water (60 mL). The resulting organic phase was separated from the resulting aqueous phase, and the aqueous phase was washed with toluene. The combined organic extracts were washed with 120 mL of 7 volume % HCl. The combined extracts were concentrated under reduced pressure (25 torr), and the resulting crude product was distilled (b.p. 58-65°C at 0.01 torr) to give 33.8 g of (S)-8-(2-(2-(2-(trifluoromethoxy(tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-7-fluorooct-1-ene.

Preparation of Starting Material:

4-(5-Octylpyrimidine-2-yl)phenyl Nonafluorobutane Sulfonate

A 12 liter flask fitted with a mechanical stirrer, a constant addition funnel, a thermometer, and a reflux condenser was charged with of 5-octyl-2-(4-hydroxyphenyl)pyrimidine (300 g, 1.05 mol), perfluorobutanesulfonyl fluoride (378 g, 1.25 mol), and tert-butylmethylether (3 L) under positive nitrogen pressure and was cooled with an ice bath to 16°C. 1,8-Diazabicyclo[5.4.0]undec-7-ene (180 g, 1.18 mol) was added to the resulting mixture over 25 minutes, while maintaining the temperature of the mixture below 20°C. After the addition was complete, the mixture was stirred at room temperature for 2 hours, and then 3 liters of water was added. The resulting aqueous phase was separated from the resulting organic phase, and the organic phase was washed with a mixture of 2.25 liters of water and 0.75 liters of concentrated HCl. The solvent was removed from the organic phase under reduced pressure to yield 697 g of crude product, which was recrystallized from ethanol to yield 4-(5-octyl

pyrimidine-2-yl)phenyl nonafluorobutane sulfonate (499 g, 84% yield).

Preparation of Product:

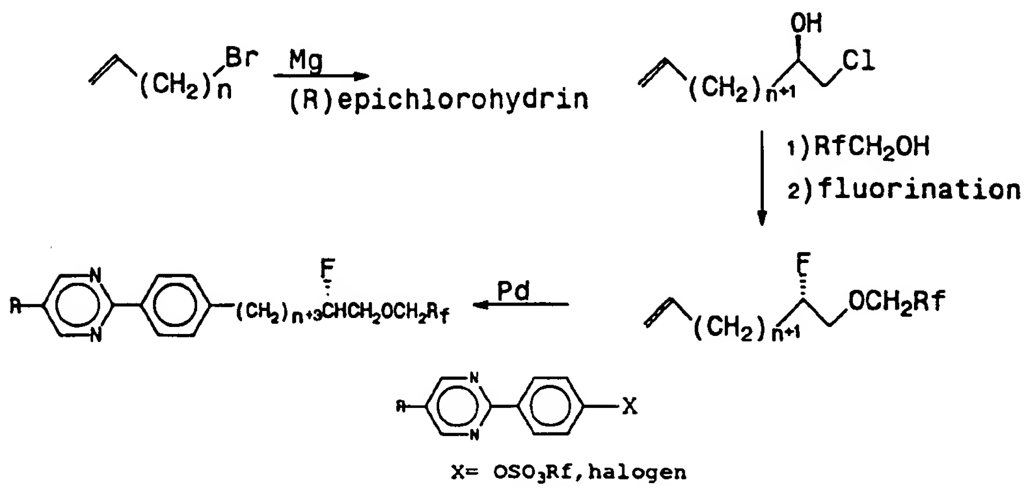
A 1 liter flask fitted with a magnetic stirring bar, a thermocouple, and a nitrogen inlet was charged with anhydrous tetrahydrofuran (230 mL) and 9-borabicyclo[3.3.1]nonane (229 mL, 0.5 M in THF) under a nitrogen atmosphere. The resulting solution was cooled to 5°C and then (S)-8-(2-(2-(2-(trifluoromethoxy(tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-7-fluorooct-1-ene (50 g, 95.4 mmol) was added via syringe at a rate such that the temperature of the resulting mixture was maintained below 7°C. The mixture was stirred for 14 hours, and then $PdCl_2(Ph_3P)_2$ (2.0 g, 2.86 mmol), NaOH (11.4 g, 286.1 mmol), and 4-(5-octyl pyrimidine-2-yl)phenyl nonafluorobutane sulfonate (54.0 g, 95.4 mmol) were added. The resulting mixture was heated to 50°C for 1.5 hours and was then poured into 1 liter of water. The resulting product was extracted with toluene (3x100 mL), and the toluene extracts were washed with water (3x100 mL). The solvent was removed under reduced pressure, and the resulting crude brown product was chromatographed through 200 g of silica gel (10 volume % ethyl acetate in heptanes eluent) and was further purified by recrystallization from heptane at -20°C followed by Kugelrohr distillation (b.p. 195 - 197°C at 0.02 torr; yield 54.7 g).

Examples 2 through 140

Example 2 - 140 were prepared essentially as described in Example 1 using homologous starting materials according to the following general Scheme 1

(where n is an integer of 0 to 7 and R_f and R are as defined above for Formula I.

Scheme 1



<u>Example 141</u>

Preparation of 5-Hexyloxy-2-[4(-6-(2-pentafluoroethoxy)-2,2-difluoroethoxy)-(S)-7-fluorooctyl)phenyl]pyrimidine

The starting material, 5-hexyloxy-2-[4(-6-(2-pentafluoroethoxy)-2,2-difluoroethoxy)-(R)-7-hydroxyoctyl)phenyl]pyrimidine, was prepared by combining 5-hexyloxy-2-[4-(1,2-epoxyhexyl)phenyl]pyrimidine (3.0 g, 7.85 mmol; which can be prepared from (R)-1,2-epoxy-7-octene and 4-(5-hexyloxypyrimidine-2-yl)phenyl trifluoromethanesulfonate by the method described in Oh-e, T. et. al., J. Org. Chem. <u>58</u>, 2201 (1993).), 2-pentfluoroethoxy-2,2-difluoroethanol (2.04 g, 9.42 mmol), Adogen™ 464 (0.4 mL), potassium hydroxide (1.0 mL 50 weight % in H_2O), and THF (1 mL). The resulting mixture was heated at 75°C for 12 hours. The resulting

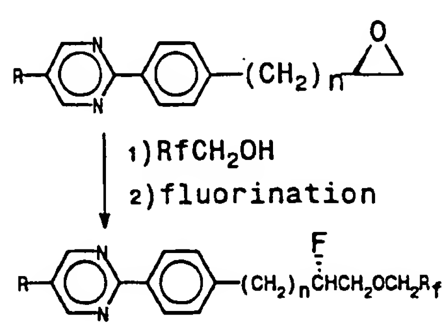
alcohol was purified by recrystallization from acetonitrile (yield 3.99 g).

The title compound was prepared by dropwise addition of 5-hexyloxy-2-[4(-6-(2-pentafluoroethoxy)-2,2-difluoroethoxy)-(R)-7-hydroxyoctyl)phenyl]pyrimidine (3.99 g, 6.68 mmol) in THF (13 mL) to a solution of diethylaminosulfur trifluoride (1.2 g, 7.35 mmol) in THF (22 mL) at -50°C. The resulting mixture was then warmed to 0°C and subsequently cooled to -50°C before addition of pyridine (1.1 mL). The mixture was stirred at room temperature for 12 hours and was then added to a slurry of silica gel (15 g in 100 mL diethyl ether). Solvent was removed under reduced pressure, and the resulting product was purified by column chromatography (silica gel), eluting with 10:1 hexane/ethyl acetate, followed by Kugelrohr distillation (b.p. 156-165°C at 0.1 torr; yield 0.93 g).

<u>Examples 142 through 163</u>

Examples 142 - 163 were prepared essentially as described in Example 141 using homologous materials as shown in the following general Scheme 2. In Scheme 2, n is an integer of 4 to 6, and R_f and R are as defined above for Formula I.

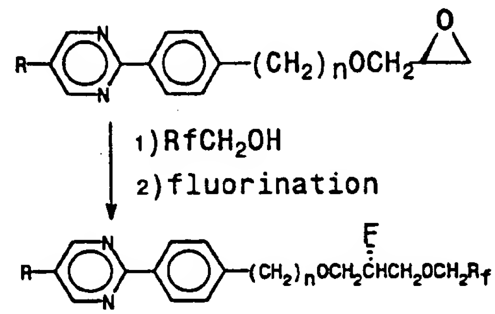
Scheme 2



Examples 164 through 175

Examples 164 - 175 were prepared essentially as described in Example 141 using (S) 3-(3-butenyloxy)-1,2-epoxy-propane (prepared from (R) epichlorohydrin and 3-buten-1-ol using $BF_3 \cdot Et_2O$ and subsequent treatment with base) in place of (R)-1,2-epoxy-7-octene according to the following general Scheme 3. In Scheme 3, n is an integer of 4, and R_f and R are as defined above for Formula I.

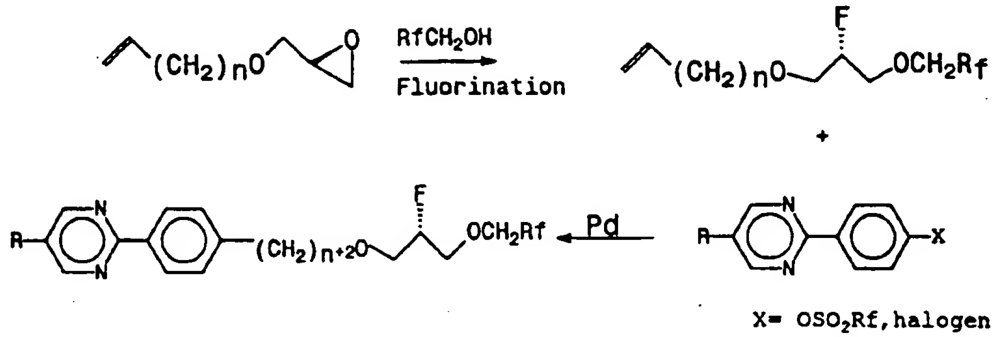
Scheme 3



Examples 176 through 186

Examples 176 - 186 were prepared essentially as described in Example 1 using (R) 1-chloro-3-(5-hexenyloxy)- 2-propanol (prepared from (R) epichlorohydrin and 5-hexen-1-ol using $BF_3 \cdot Et_2O$) in place of (R)1-chloro-7-octen-2-ol according to the following general Scheme 4 (where n is an integer of 4 to 6, and R and R_f are as defined above for Formula I):

Scheme 4



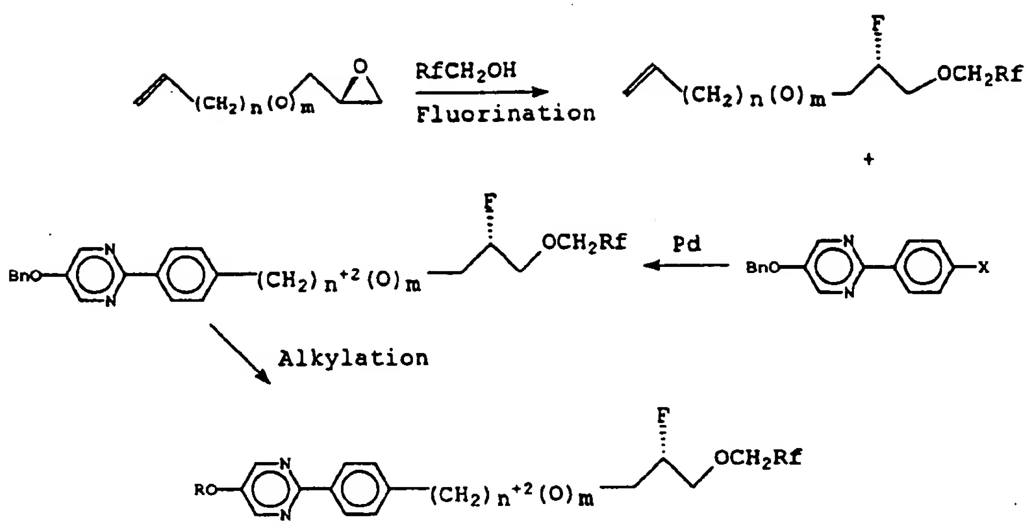
Example 187

Example 187 was prepared essentially as described in Example 1 using (S) 1-chloro-3-(5-octenyloxy)- 2-propanol (prepared from (R) epichlorohydrin and 7-octen-1-ol using $BF_3 \cdot Et_2O$) in place of (R) 1-chloro-7-octen-2-ol.

Examples 188 through 201

Examples 188 - 201 were prepared essentially as described in Example 176 using 5-benzyloxy-2-(4-trifluoromethanesulfonyloxyphenyl) pyrimidine in place of 5-octyloxy-2-(4-nonafluorobutanesulfonyloxyphenyl) pyrimidine. The resulting compound was treated with 10 weight % palladium on carbon under hydrogen pressure (3100 torr) to obtain 5-hydroxy-2-[4-(6-(3-(2-(2-(2-(trifluoromethoxy(tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-2-fluoropropyloxy)hexyl)phenyl]pyrimidine. This material was then treated under basic conditions with the corresponding chloride or methane sulfonate to give the final products. The procedure is shown in the following general Scheme 5 (where Bn is a benzyl protecting group, n is an integer of 3 or 4, m is an integer of 0 or 1, and R_f and R are as defined above for Formula I):

Scheme 5



Example 202

Preparation of 5-Octyloxy-2-[4-(2-(3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(R)-2-fluoropropoxy)ethoxy)phenyl]pyridine

The title compound was prepared by combining 5-octyloxy-2-[4-hydroxyphenyl]pyrimidine (2.2 g, 7.4 mmol), 2-(3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(R)-2-hydroxypropoxy)ethyl chloride (4.2 g, 7.4 mmol), and potassium carbonate (1.2 g, 8.9 mmol) in a 1:1 mixture of acetonitrile and dimethyl formamide. After heating overnight, the resulting mixture was poured into deionized water (40 mL), was filtered, and the resulting product purified by chromatography, eluting with 4:1 and then 2:1 hexane/ethyl acetate (yield 2.56 g). The resulting chiral (R)-hydroxy compound (2.5 g, 3.0 mmol) was treated with diethylaminosulfur trifluoride (0.58 g, 3.6 mmol) to produce the title compound, which was purified by recrystallization from ethanol, followed by

Kugelrohr distillation (b.p. 210-20°C at 0.4 torr; yield 1.42 g).

Example 203

Preparation of 5-heptyl-2-[4-(3-(3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-2-fluoropropoxy)propoxy)phenyl]pyrimidine

The starting material, 3-(3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-2-fluoropropoxy)propyl chloride, was prepared by combining 3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-2-fluoropropanol (20 g, 39.4 mmol) and 1-bromo-3-chloropropane (18.6 g, 118 mmol). The resulting compound (2.0 g, 3.4 mmol) was then combined with 5-heptyl-2-(4-hydroxyphenyl)pyrimidine (0.9 g, 3.4 mmol) in acetonitrile/dimethyl formamide (1:1, 20 mL) using essentially the procedure of Example 8 of International Patent Publication No. WO 96/33251. The resulting crude product was further purified by chromatography, eluting with 30:1 toluene/ethyl acetate, followed by Kugelrohr distillation (180-90°C at 0.01 torr; yield 0.96 g).

Example 204

Preparation of 5-Hexyloxy-2-[4-(3-(3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-2-fluoropropoxy)propoxy)phenyl]pyrimidine

The title compound was prepared essentially as described in Example 8 of International Patent Publication No. WO 96/33251 by combining 3-(3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-2-fluoropropoxy)propyl chloride

(3.0 g, 5.1 mmol) with 5-hexyloxy-2-(4-hydroxyphenyl)pyrimidine (1.4 g, 5.1 mmol). The resulting crude product was purified by Kugelrohr distillation (b.p. 170-80°C at 0.01 torr).

Example 205

Preparation of 5-Octyloxy-2-[4-(4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluorobutoxy)phenyl]pyrimidine

The starting material, 4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluorobutane-1-methanesulfonate, was prepared by the following procedure: 4-benzyloxy-(R)-1,2-epoxybutane (8.0 g, 44.9 mmol, prepared essentially as described by J. A. Frick in Synthesis 7, 621 (1992)) was combined with 2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy (23.3 g, 53.9 mmol), potassium hydroxide (3.0 g, 53.9 mmol, aqueous) in tetrahydrofuran (3 mL) and refluxed for 3 hours to produce 4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(R)-3-hydroxybutane-1-methanesulfonate. This (R)-hydroxy compound (20 g, 32.8 mmol) was treated with diethylaminosulfur tetrafluoride (6.3 g, 39.3 mmol) and was then hydrogenated using $Pd(OH)_2$ on carbon to remove the benzyl protecting group.

The title compound was prepared by combining 5-octyloxy-2-(4-hydroxyphenyl)pyrimidine (1.1 g, 3.8 mmol) and 4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluorobutane-1-methanesulfonate (2.3 g, 3.8 mmol) using essentially the procedure of Example 8 of International Patent Publication No. WO 96/33251. The resulting crude product was further

purified by chromatography, followed by Kugelrohr distillation (yield 1.92 g).

Example 206

Preparation of 5-Hexyloxy-2-[3-(4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluorobutoxy)propyl)phenyl]pyrimidine

The title compound was prepared by adding (nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluorobutoxy)prop-1-ene (3.5 g, 6.2 mmol, prepared by addition of 3-bromopropene to 4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluorobutanol) to a mixture of 5-hexyloxy-2-[trifluoromethylsulfonyloxyphenyl]pyrimidine (2.5 g, 6.22 mmol), 9-borabicyclononane (12.4 mL of 0.5 M in THF), $PdCl_2dPPF$ ([1,1'-bis(diphenylphosphino)-ferrocene]palladium(II) chloride, 50 mg, 0.062 mmol), and K_3PO_4 (2.8 g, 13.1 mmol) in dioxane (17 mL) at a temperature less than 5°C. After stirring the resulting mixture at 100°C for 16 hours, water was added, and the mixture was extracted with toluene. The combined toluene extracts were dried, and the resulting crude product was purified by chromatography, eluting first with 10:1 then 4:1 hexanes/ethyl acetate, followed by Kugelrohr distillation (b.p. 180°C at 0.01 torr; yield 0.95 g).

Example 207

Preparation of 5-Octyloxy-2-[1-(4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluorobutoxy)methyl)phenyl]pyrimidine

The title compound was prepared by combining 2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-

difluoroethoxy)-(S)-3-fluorobutanol (2.0 g, 3.8 mmol), 5-octyloxy-2-[bromomethylphenyl]pyrimidine (prepared essentially as described in EP 474196, 1.44 g, 3.8 mmol), potassium hydroxide (0.21 g, 3.8 mmol), and Adogen™ 464 (0.15 g) in tetrahydrofuran and then heating the resulting mixture overnight at 75°C. The resulting crude product was purified by chromatography, eluting with 8:1 hexanes/ethyl acetate, followed by Kugelrohr distillation (yield 0.45 g).

<u>Example 208</u>

Preparation of 5-Hexyloxy-2-[4-(4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluorobutoxy)butoxy)phenyl]pyrimidine

The starting material, 4-(4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluorobutoxy)butyl bromide, was prepared by combining 1,4-dibromobutane (4.9 g, 22.8 mmol) with 2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluorobutanol (4.0 g, 7.6 mmol). The title compound was prepared essentially as described in Example 8 of International Patent Publication No. WO 96/33251 by combining 4-(4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluorobutoxy)butyl bromide (2.7 g, 4.1 mmol) with 5-hexyloxy-2-(4-hydroxyphenyl)pyrimidine (1.1 g, 4.1 mmol). The resulting crude product was purified by chromatography, eluting with 6:1 hexanes/ethyl acetate (yield 0.58 g).

<u>Example 209</u>

Preparation of 5-Octyl-2-[4-(4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-

difluoroethoxy)-(S)-3-fluorobutoxy)butoxy)phenyl]pyrimidine

The title compound was prepared essentially as described in Example 8 of International Patent Publication No. WO 96/33251 by combining 4-(4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluorobutoxy)butyl bromide (2.6 g, 3.95 mmol) with 5-octyl-2-(4-hydroxyphenyl)pyrimidine (1.1 g, 3.95 mmol). The resulting crude product was purified by chromatography, eluting with 6:1 hexanes/ethyl acetate (yield 2.4 g).

Example 210

Preparation of 5-Heptyl-2-[4-(7-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(R)-6-fluoroheptyloxy)phenyl]pyrimidine

The starting material, 7-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(R)-6-fluoroheptane-1-methanesulfonate, was prepared by the following procedure: 7-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(R)-6-fluorohept-1-ene (10 g, 18.8 mmol) was treated with $BH_3 \cdot THF$ (9.4 mmol) in tetrahydrofuran, followed by oxidation with hydrogen peroxide (30% aqueous, 9.4 mmol) to produce the corresponding heptanol. This heptanol (8.9 g, 15.7 mmol) was treated with methanesulfonyl chloride (1.98 g, 17.3 mmol) to produce the methanesulfonate derivative

The title compound was prepared by combining 5-heptyl-2-(4-hydroxyphenyl)pyrimidine (1.1 g, 3.8 mmol) and 4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluoropropoxy)butane-1-methanesulfonate (2.3 g, 3.8 mmol) essentially as described in Example 8 of International Patent

Publication No. WO 96/33251. The resulting crude product was further purified by recrystallization from heptane, then from ethanol, followed by Kugelrohr distillation (b.p. 200°C at 0.1 torr; yield 1.79 g).

Example 211

Preparation of 5-Hexyloxy-2-[4-(7-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(R)-6-fluoroheptyloxy)phenyl]pyrimidine

The title compound was prepared by combining 5-hexyloxy-2-(4-hydroxyphenyl)pyrimidine (0.36 g, 1.32 mmol) and 4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluoropropoxy)butane-1-methanesulfonate (0.85 g, 1.32 mmol) essentially as described in Example 8 of International Patent Publication No. WO 96/33251. The resulting crude product was further purified by chromatography, eluting with 10:1 hexanes/ethyl acetate, followed by Kugelrohr distillation (b.p. 190-210°C at 0.01 torr; yield 0.67 g).

Example 212

Preparation of 5-Octyloxy-2-[4-(7-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(R)-6-fluoroheptyloxy)-2,3-difluorophenyl]pyrimidine

The title compound was prepared essentially as described in Example 211 by combining 5-octyloxy-2-(4-hydroxyphenyl)-2,3-difluoropyrimidine and 4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluoropropoxy)butane-1-methanesulfonate essentially as described in Example 8 of International Patent Publication No. WO 96/33251. The resulting crude product was further purified by

chromatography, eluting with 10:1 hexanes/ethyl acetate, followed by Kugelrohr distillation.

Example 213

Preparation of 5-Octyloxy-2-[4-(7-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(R)-6-fluoroheptyloxy)-2,3-difluorophenyl]pyrimidine

The title compound was prepared essentially as described in Example 211 by combining 5-octyloxy-2-(4-hydroxyphenyl)-3-fluoropyrimidine and 4-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-3-fluoropropoxy)butane-1-methanesulfonate essentially as described in Example 8 of International Patent Publication No. WO 96/33251. The resulting crude product was further purified by chromatography, eluting with 10:1 hexanes/ethyl acetate, followed by Kugelrohr distillation.

Example 214

Preparation of 5-(2-(S)-Fluorodecyloxy-2-[4-(6-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-5-fluorohexyl)phenyl]pyrimidine

The title compound was prepared by adding (nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-5-fluorohex-1-ene (4.0 g, 7.5 mmol) to a mixture of 5-(2-(S)-fluorodecyloxy-2-[6-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-5-fluorohexyl)phenyl]pyrimidine (3.6 g, 7.5 mmol), 2-(2, 9-borabicyclononane (15 mL of 0.5 M in THF), $PdCl_2dPPF$ (60 mg, 0.075 mmol), and K_3PO_4 (3.3 g, 15.8 mmol) in dioxane (17 mL) at a temperature less than 5°C. After stirring the resulting mixture at room temperature overnight, water was added, and the mixture was extracted with toluene. The combined

toluene extracts were dried, and the resulting crude product was purified by chromatography, eluting with 10:1 hexanes/ethyl acetate, followed by Kugelrohr distillation (b.p. 190-210°C at 0.01 torr) and recrystallization from heptane (yield 2.2 g).

Example 215

Preparation of 5-Hexyloxy-2-[4-(3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy))-(R)-2-fluoropropyloxy)-(R)-2-methylpropyloxy)phenyl]pyrimidine

The starting material, 3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy))-(R)-2-fluoropropyloxy)-(R)-2-methylpropane-1-methanesulfonate, was prepared as follows: (S)-2-methyl-3-bromopropanol was alkylated with benzyl bromide to produce (S)-2-methyl-3-bromo-1-benzyloxypropane, which was then combined with 3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy))-(R)-2-fluoropropanol, followed by hydrogenation with 10% Pd/C to remove the benzyl protecting group. The title compound was prepared by combining 5-hexyloxy-2-(4-hydroxyphenyl)pyrimidine (0.7 g, 2.58 mmol) and 3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy))-(R)-2-fluoropropyloxy)-(R)-2-methylpropane-1-methanesulfonate (1.7 g, 2.58 mmol) essentially as described in Example 8 of International Patent Publication No. WO 96/33251. The resulting crude product was further purified by chromatography, eluting with 10:1 hexanes/ethyl acetate, and was recrystallized from heptane, followed by Kugelrohr distillation (b.p. 180-190°C at 0.02 torr; yield 1.28 g).

Example 216

Preparation of 5-Heptyloxy-2-[4-(3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy))-(S)-1-(trifluoromethyl)ethyl)propyl)phenyl]pyrimidine

The title compound was prepared by adding 3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy))-(S)-1-(trifluoromethyl)ethyl)prop-1-ene (6.0 g, 10.3 mmol, prepared by addition of 3-bromopropene to 2-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(S)-1-(trifluoromethyl)ethanol) to a mixture of 5-heptyloxy-2-[trifluoromethylsulfonyloxyphenyl]pyrimidine (4.3 g, 10.3 mmol), 9-borabicyclononane (20.6 mL of 0.5 M in THF), $PdCl_2dPPF$ (82 mg, 0.1 mmol), and K_3PO_4 (2.8 g, 13.1 mmol) in dioxane (17 mL) at a temperature less than 5°C. After stirring the resulting mixture at 100°C for 16 hours, water was added, and the mixture was extracted with toluene. The combined toluene extracts were dried, and the resulting crude product was purified by chromatography, eluting with 10:1 hexanes/ethyl acetate, and was recrystallized from heptane, followed by Kugelrohr distillation (b.p. 160-70°C at 0.02 torr; yield 3.04 g).

Example 217

Preparation of 5-Hexyloxy-2-[4-(2-(2-(2-(trifluoromethoxy)tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(R)-8-fluorononyloxy)phenyl]pyrimidine

The starting material, 2-(2-(2-(trifluoromethoxy)tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(R)-8-fluorononyl-1-methanesulfonate, was prepared by hydroboration of 2-

(2-(2-(trifluoromethoxy)tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)-(R)-8-fluoronon-1-ene using BH_3 in tetrahydrofuran, followed by mesylation of the resulting nonanol. The title compound was prepared by combining 5-hexyloxy-2-(4-hydroxyphenyl)pyrimidine (2.0 g, 7.8 mmol) and 2-(2-(2-(trifluoromethoxy)tetrafluoroethoxy) tetrafluoroethoxy)-2,2-difluoroethoxy)-(R)-8-fluorononyl-1-methanesulfonate (4.9 g, 7.8 mmol) essentially as described in Example 8 of International Patent Publication No. WO 96/33251. The resulting crude product was further purified by recrystallization from hexanes, followed by chromatography (eluting with 10:1 hexanes/ethyl acetate) and then by Kugelrohr distillation (b.p. 185-95°C at 0.01 torr; yield 2.3 g).

Example 218

Preparation of 5-Heptyloxy-2-(4-[5-(3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy))-(S)-2-(fluoropropoxy)-2,2,3,3,4,4-hexafluoropentyloxy)phenyl]pyrimidine

The title compound was prepared essentially as in Example 97 of International Patent Publication No. 96/15092 by combining 5-heptyloxy-2-(4-hydroxyphenyl)pyrimidine with 5-(3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy))-(S)-2-(fluoropropoxy)-2,2,3,3,4,4-hexafluoropentyl-1-butanesulfonate. The resulting product was purified by chromatography, followed by Kugelrohr distillation (b.p. 200-5°C at 0.008 torr).

Example 219

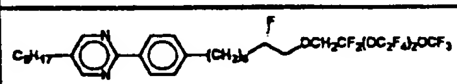
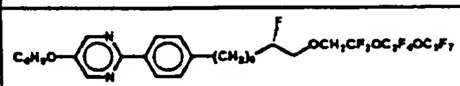
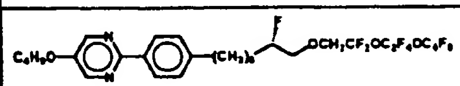
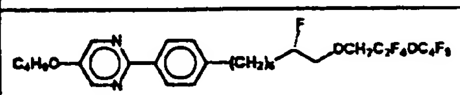
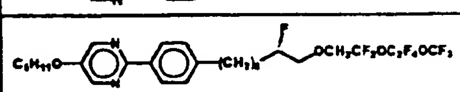
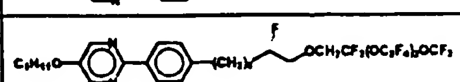
Preparation of 5-Heptyloxy-2-(4-[4-(3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-

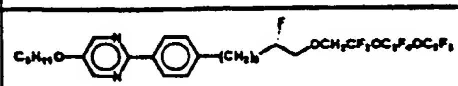
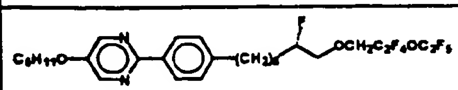
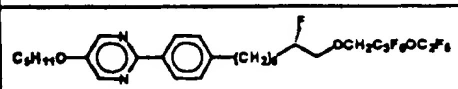
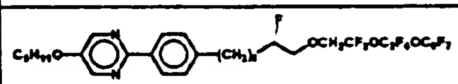
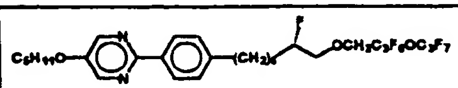
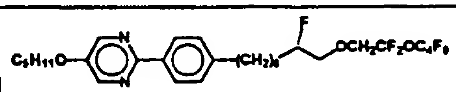
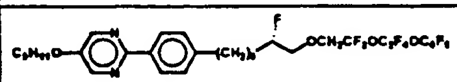
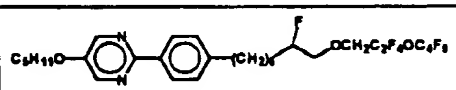
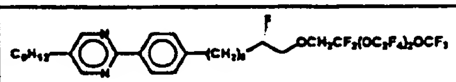
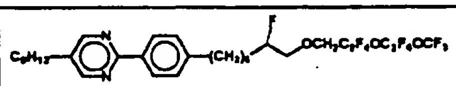
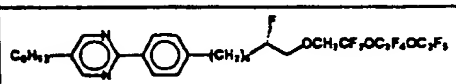
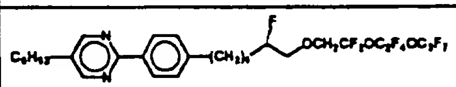
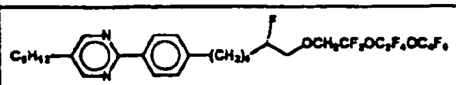
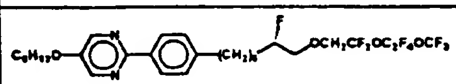
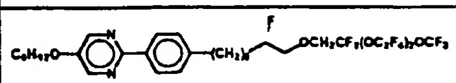
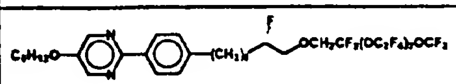
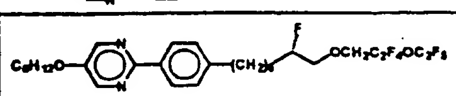
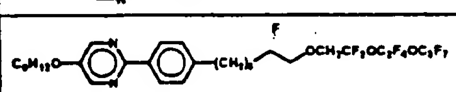
difluoroethoxy))-(S)-2-(fluoropropoxy)-2,2,3,3,-tetrafluorobutyloxy)phenyl]pyrimidine

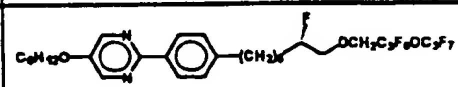
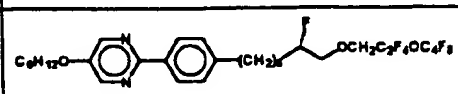
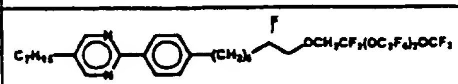
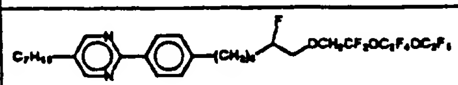
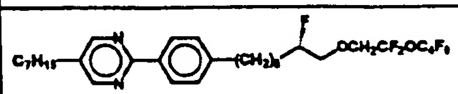
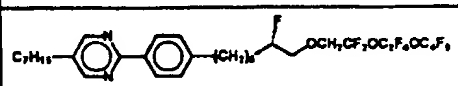
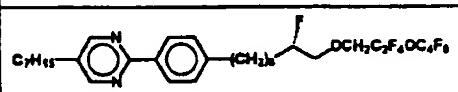
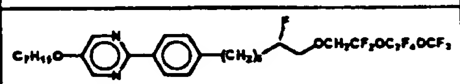
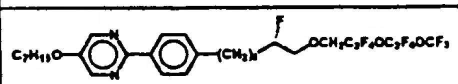
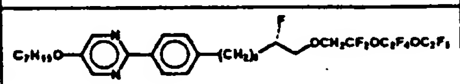
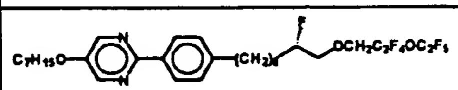
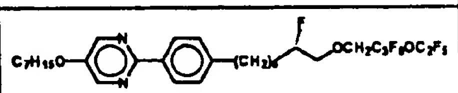
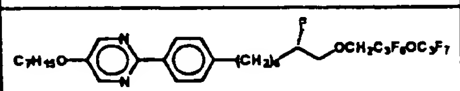
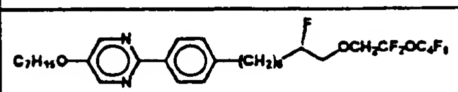
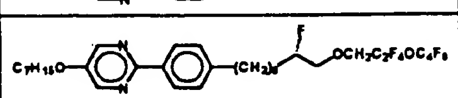
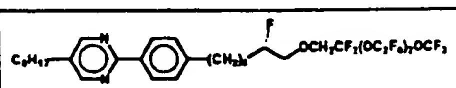
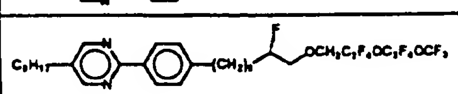
The title compound was prepared essentially as in Example 97 of International Patent Publication No. 96/15092 by combining 5-heptyloxy-2-(4-hydroxyphenyl)pyrimidine with 4-(3-(2-(2-(nonafluorobutoxy)tetrafluoroethoxy)-2,2-difluoroethoxy))-(S)-2-(fluoropropoxy)-2,2,3,3-tetrafluorobutyl-1-butanesulfonate. The resulting product was purified by chromatography, followed by Kugelrohr distillation (b.p. 195-200°C at 0.01 torr).

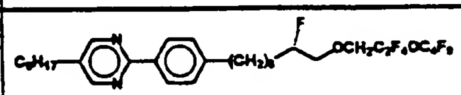
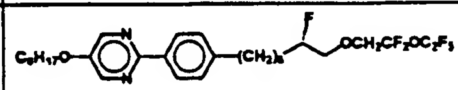
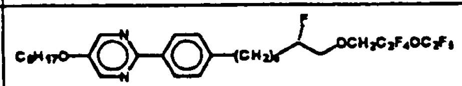
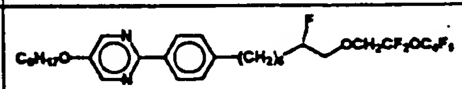
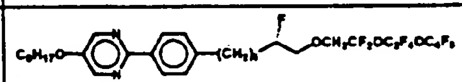
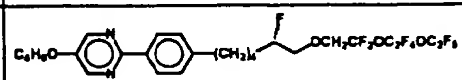
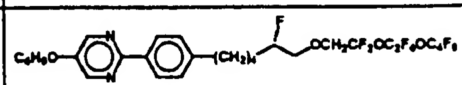
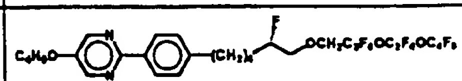
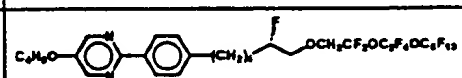
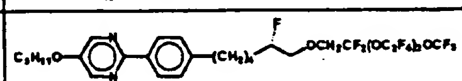
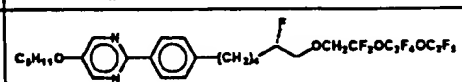
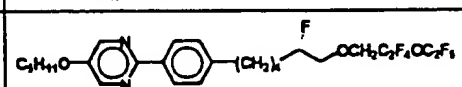
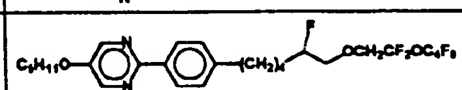
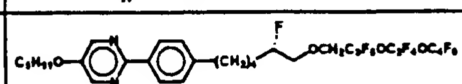
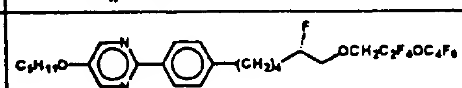
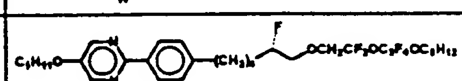
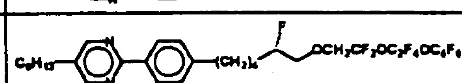
The compounds of the Examples were evaluated for transition temperatures by differential scanning calorimetry (DSC) and/or optical observation of material phase changes using a hot stage and a polarizing microscope. The transition temperatures (°C) were obtained upon cooling through the isotropic state (I) to the smectic A mesophase (S_A), the smectic C mesophase (S_C), and higher order mesophases (M1 and M2) and are set forth in Table 1 below.

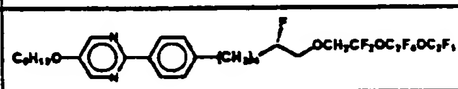
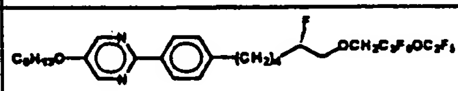
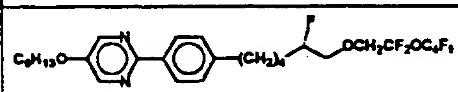
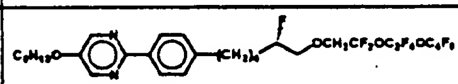
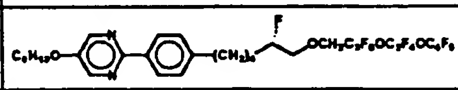
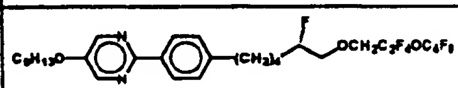
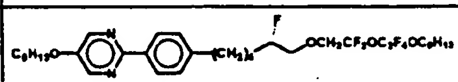
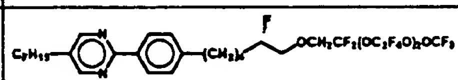
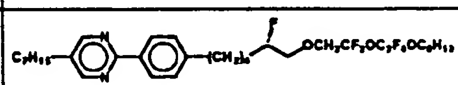
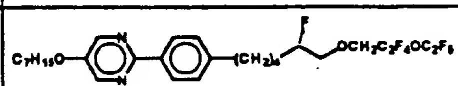
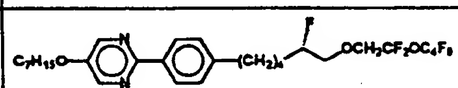
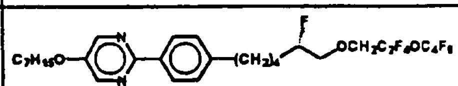
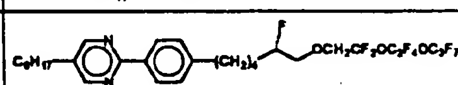
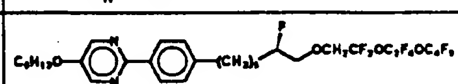
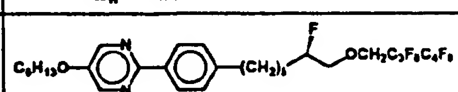
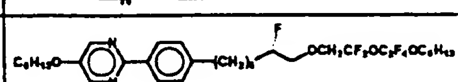
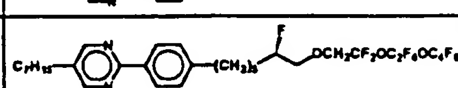
Table 1.

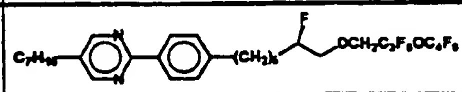
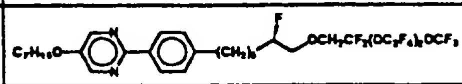
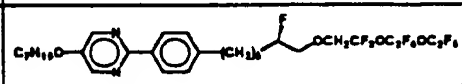
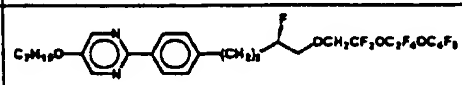
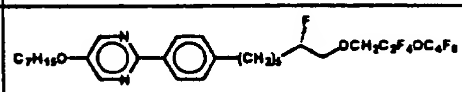
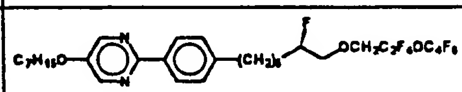
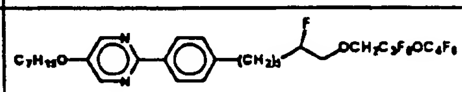
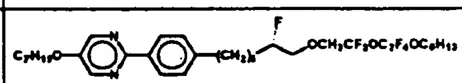
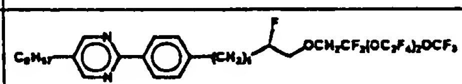
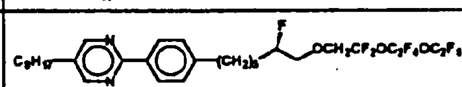
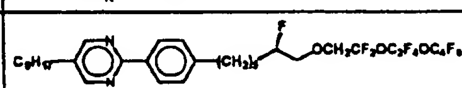
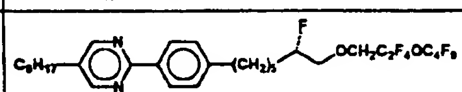
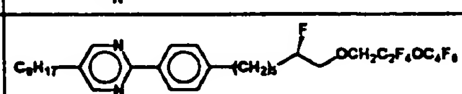
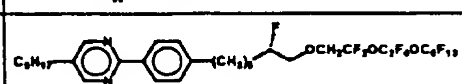
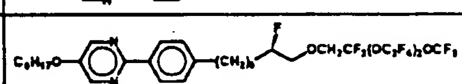
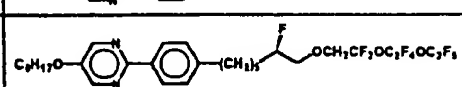
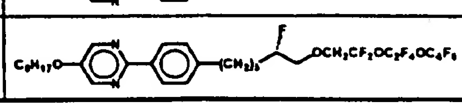
Ex. No.	Structure	I to S_A	to S_C	to S_{M1}	to K	to S_C	to S_A
1		79.3	56.7	-4.2		22.2	59.2
2		90.9	61.3	41.5		46.6	63.2
3		92.3	70.1	43.2		48.2	72.5
4		92.1	57.6	41.1		52.8	59.5
5		83.4		34.3			48.7
6		95	61	27.7		37.7	63.3

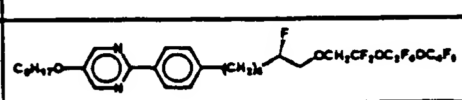
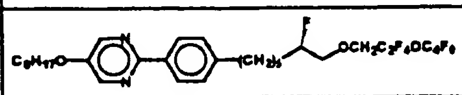
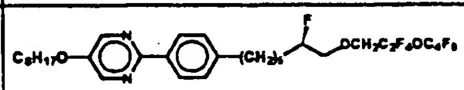
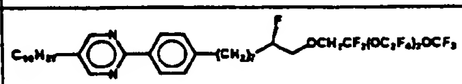
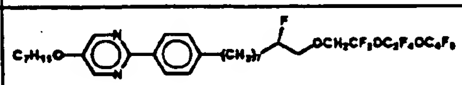
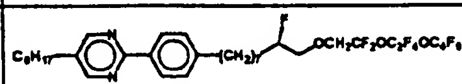
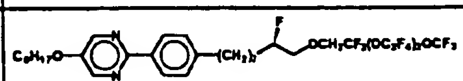
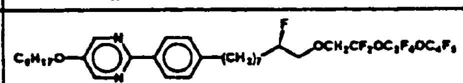
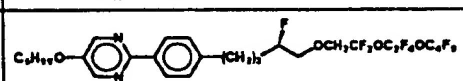
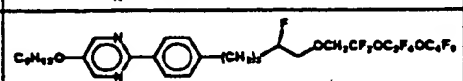
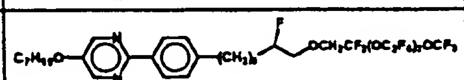
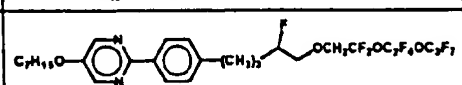
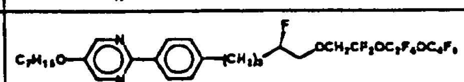
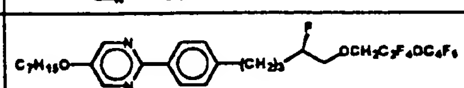
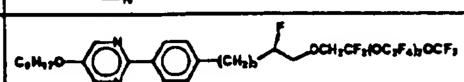
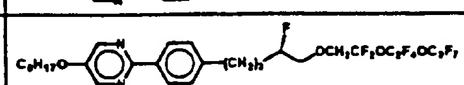
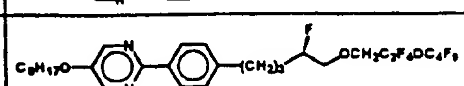
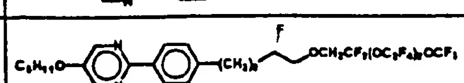
Ex. No.	Structure	I to S_A	to S_C	to S_{M1}	to K	to S_C	to S_A
7		89.6		32.4			45.2
8		84.1		30			47.9
9		95	50	38			
10		91.7	59.7	25.8		34.1	62
11		98.4	63.6	34		42.7	65.9
12		83.5		29.9			42.9
13		93.1	69.6	27.4		34.7	72.1
14		91.5	54.8	23.5		40.8	57.6
15		72.8	40.9	21.4		33.9	43.6
16		67.2	31.5	17.2		25	33.9
17		65.9		26.1			40.5
18		67.7	38	18.2		26.6	40.3
19		72.8	48.4	19.2		26.1	51
20		92		14.9			31.3
21		103.4	74.6	12.1		33.4	76.2
22		98.3	53	19.4		41.5	
23		91.8		13.5			27.2
24		98.6	74.1	11.6		30.5	76.3

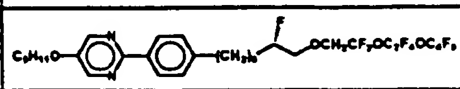
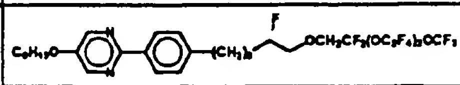
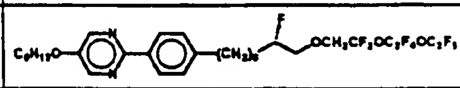
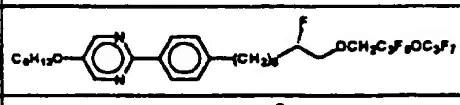
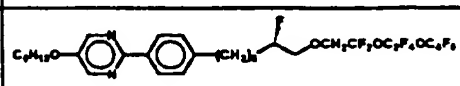
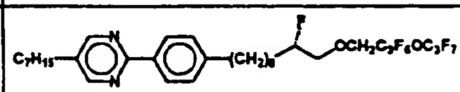
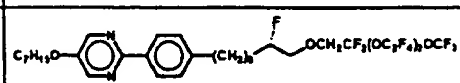
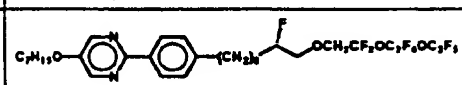
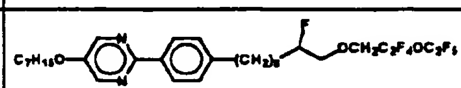
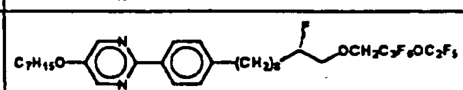
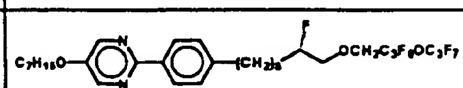
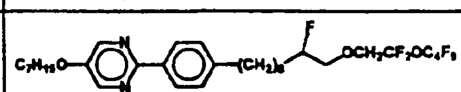
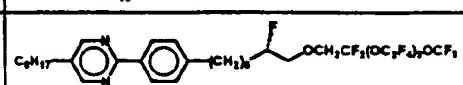
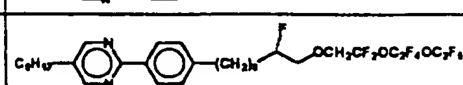
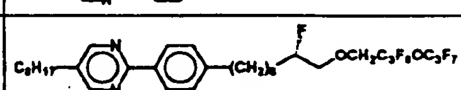
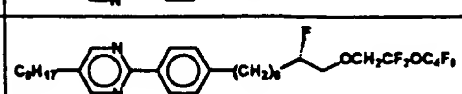
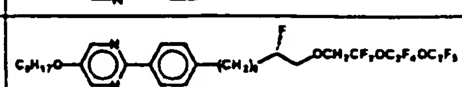
Ex. No.	Structure	I t S_A	to S_C	to S_{M1}	to K	to S_C	t S_A
25		103.1	69.6	15.3		29.9	72
26		98.1	70.3	2.6		17.6	72.6
27		80.4	46.7	8		24.8	49.4
28		73	19	13			32
29		65.4	9	7			16.3
30		78	53	<RT			
31		73.1	35.2	-1.7		21.3	37.4
32		92.4	58.1	5.9		20	60.8
33		100.3	74.7	-15.1		12.5	77.1
34		98.7	75.5	0		28.4	77.8
35		93.1	59.5	5		21.6	62
36		100	73.6	18.1		29.1	76.1
37		103.7	80.2	1.1		21	82.4
38		90.8	67.6	1.1		13.6	70.6
39		98.6	80.7	-14.9		15.3	82.8
40		78.7	50.4	-4.5		19.6	53.5
41		74	41	-0.1		22.5	45.1

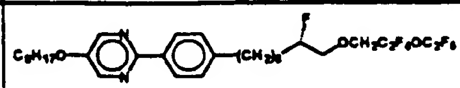
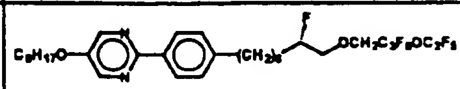
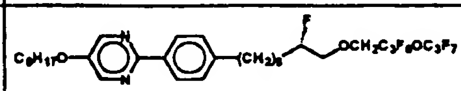
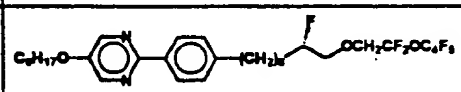
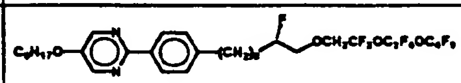
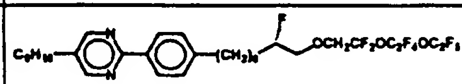
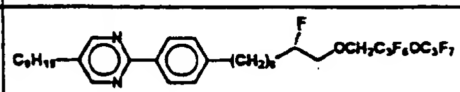
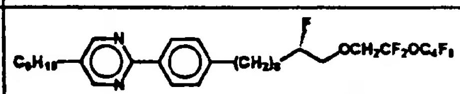
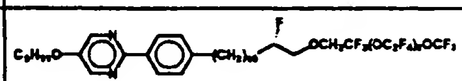
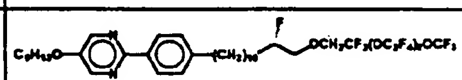
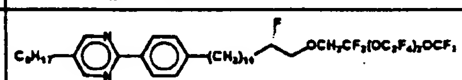
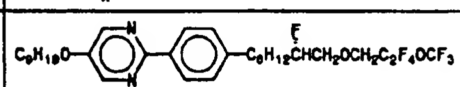
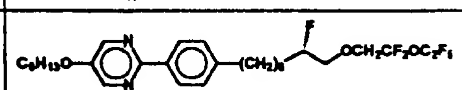
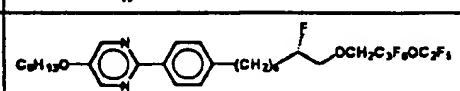
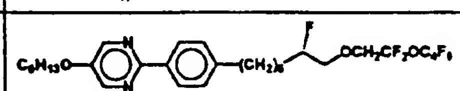
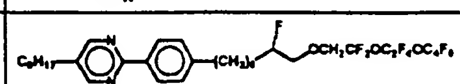
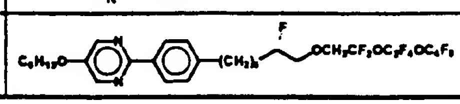
Ex. No.	Structure	I to S_A	to S_C	to S_{M1}	to K	to S_C	to S_A
42		72.5	47	-0.1		24.5	
43		88.1	61.9	-15.1		29.5	64.4
44		95.5	79.9	-12.1		18.6	82.5
45		93.8	82.2	-12.1		20.9	84.6
46		104.4	96.4	-8		-0.2	98.7
48		94.6	37	16.7			39
49		97.6	70.6	13.8		27.1	72.9
50		112.4	89.5	26.3		30	91.9
51		100.7	80.6	20.6		42.9	83.2
52		101.4	68.6	-0.4		28.9	71
53		95.2	46.4	3.2		38.5	49.1
54		88.9	5	-4.7		31.3	
55		87.6	32	-4.1		32.1	
56		112.1	89.3	43	0.7	7	91.5
57		97.3	59.2	-7.5		33.7	61.6
58		101.3	80.4	15		49.8	82.5
59		74.1	42.7	-8.1		4.9	45.2

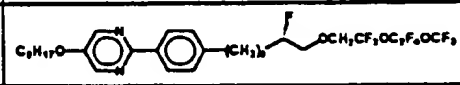
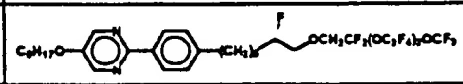
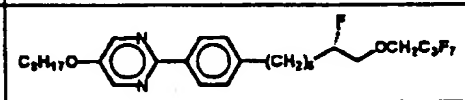
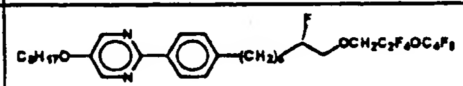
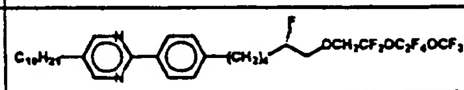
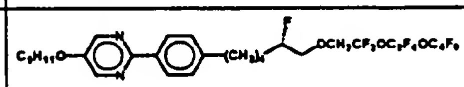
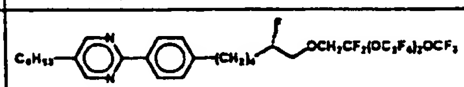
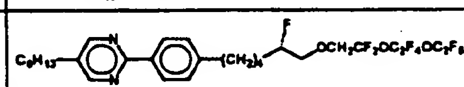
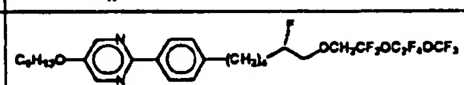
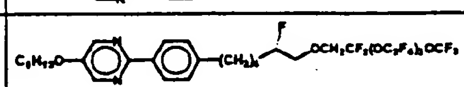
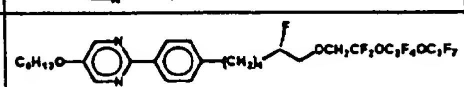
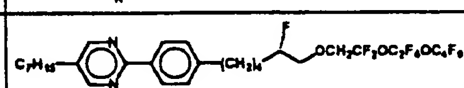
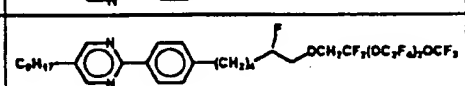
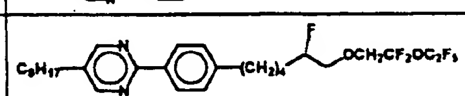
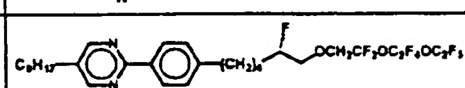
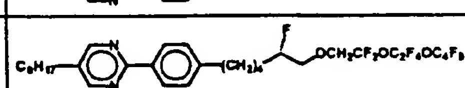
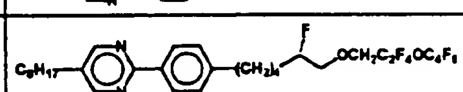
Ex. No.	Structur	I to S_A	to S_C	to S_{M1}	t K	to S_C	to S_A
60		101.5	70.3	-28		29.2	72.7
61		107.3	76.6	-23.2		7.6	79.1
62		93.6	55	-38.8		9.7	
63		105.8	81.2	-31.8		5	83.1
64		116.4	97.9	42	-29	-22	100.2
65		103.2	76.7	-38.5		-28.7	78.8
66		107.1	89.8	-24.2		23.7	92
67		81	48	-23.9		3.3	50.2
68		81.6	60.9	-19.6		18.7	63.3
69		94.3	70.4	-22.5		-12.4	72.8
70		92.6	73	-23		14.8	75.4
71		99.7	83.1	-19.9		-10.1	85.4
72		74.8	56.2	<-30		9	58.7
73		105.8		-22.8			20.8
74		109.9		-5.9			18.3
75		108.3		6.3			39.9
76		83.9		11.8			34.7

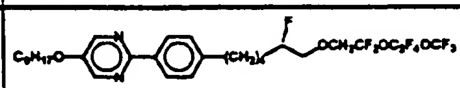
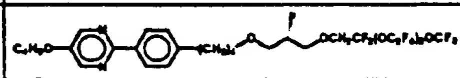
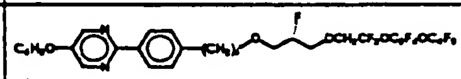
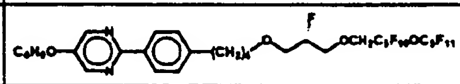
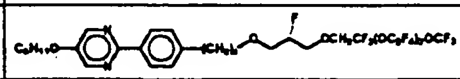
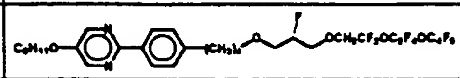
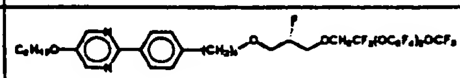
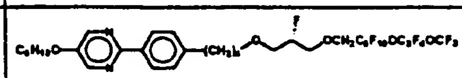
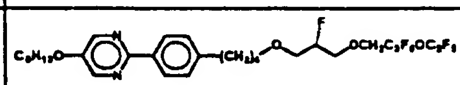
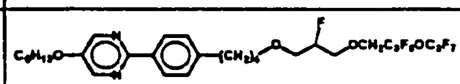
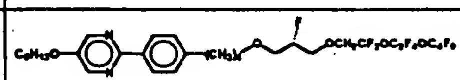
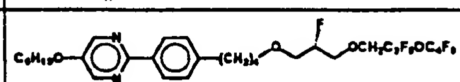
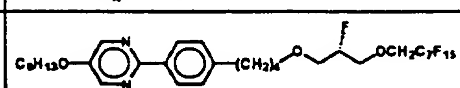
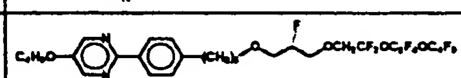
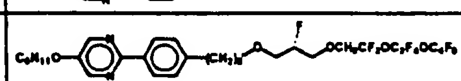
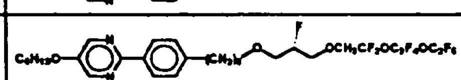
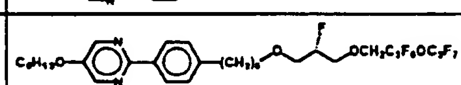
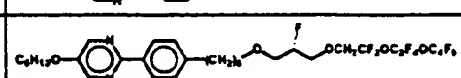
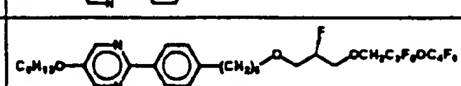
Ex. No.	Structure	I to S_A	to S_C	to S_{MI}	to K	to S_C	to S_A
77		86.7		17			34.9
78		108.1		-7.3			29.2
79		103		-5.2			36.7
80		107.9		-17.2			27.9
81		101.5	88.1	-25.3		15.8	88.6
82		102.3		-24.9			15.6
83		109.3		-9.8			24.3
84		109-2	70.7	8.6		43.5	73.7
85		84		14			36
86		78.1		17.8			44.3
87		83.2		14.5			36.8
88		77.4		2.5			23.1
89		76.7		-2.5			20.8
90		86.3		25.7			49
91		110.3	66	-17.7		28.9	
92		105.5	35	-5.3			35.4
93		108.3	72	-18		29.2	

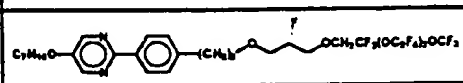
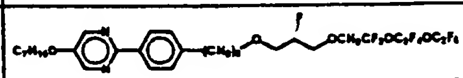
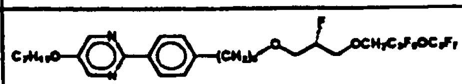
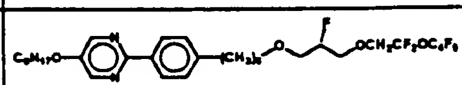
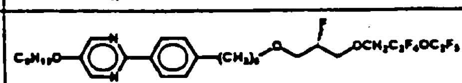
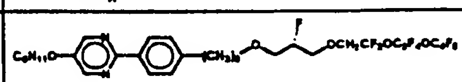
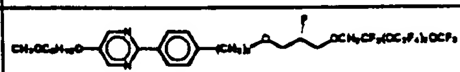
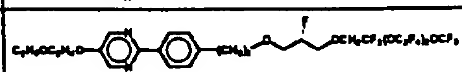
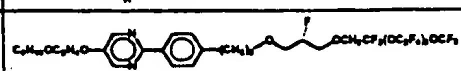
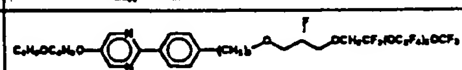
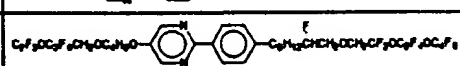
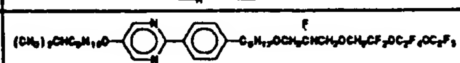
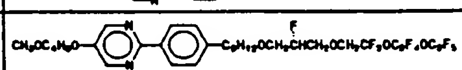
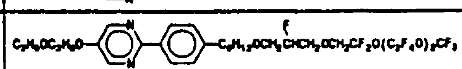
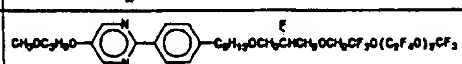
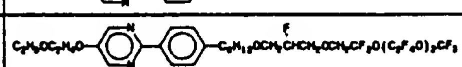
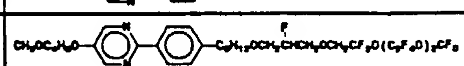
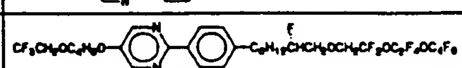
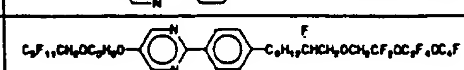
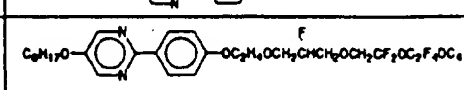
Ex. No.	Structure	I to S_A	to S_C	to S_{M1}	to K	to S_C	to S_A
94		109.7	70	-17.3		28	
95		104.6	62.7	-14.8		21.5	65.7
96		104.2	58	-15.1		20.5	
97		86.6	43.3	25.7			49.6
98		102.5		14			38.6
99		79.7		22.6			43.8
100		107.7	45	11.2		39.2	
101		106.7	80	9.4		37.8	
102		105.4		-34			9.4
103		111.4	-3.3	<-30			8.5
104		112.7	37	-15.6		23	
105		109	38.8	-13.5		27.6	41
106		109.9	77.1	-15		19	79.3
107		105.9	50.6	-11.6		-6.1	53.6
108		113.5	72.1	-10.9		23.7	73.9
109		109.7	70.6	-16.1		30.1	73.2
110		106.4	73.6	-7.1		-4.5	75.9
111		89.9	63.1	42.8		47.6	65.4

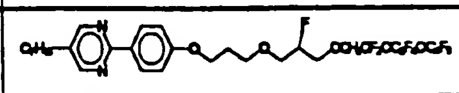
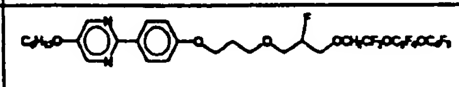
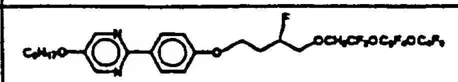
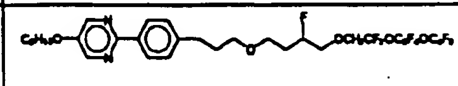
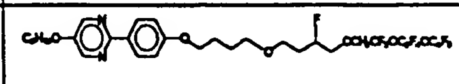
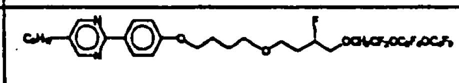
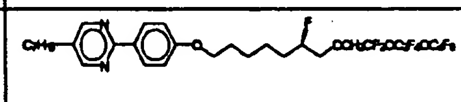
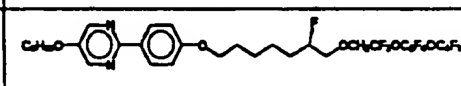
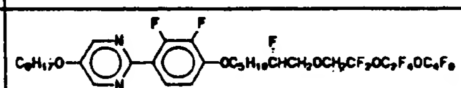
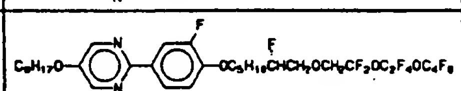
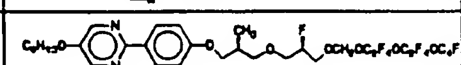
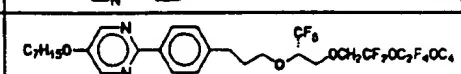
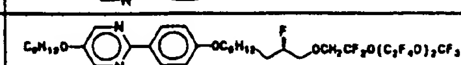
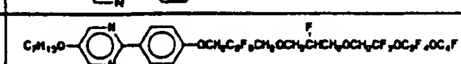
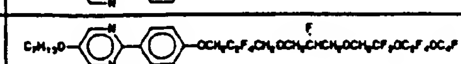
Ex. No.	Structure	I to S_A	to S_C	t S_{MI}	to K	to S_C	to S_A
112		90.5	64.9	36.8		42.2	67.2
113		98	73.6	30.4		40.2	75.9
114		91.2	33	31.2			45.6
115		96.4	62.8	35.2		42.3	64.5
116		96.2	80.7	28.5		37.1	83.2
117		75.3	46.5	28.4		35.2	48.2
118		95	77.2	23.5		39.2	79.3
119		93.5	68	18.8		46.6	69.8
120		86	37	15.5		26.8	
121		94.8	61.5	31.1		38.6	60.9
122		97.9	75.8	25.3		34.1	77.5
123		88.1	57.3	22.5		41.4	59.9
124		77.6	59.9	9.2		34	81.1
125		71.1	30	15.6			36.1
126		74.5	49.8	22		36	51.5
127		64.5	26.4	21			32.6
128		97.9	85.1	8.9		37.7	87.4

Ex. No.	Structure	I to S_A	to S_C	to S_{M1}	to K	to S_C	to S_A
129		93	69.6	-3.5		30.4	71.3
130		97.9	85.1	8.9		37.7	87.4
131		101.4	89.2	11.7		29.8	90.5
132		92.7	79.3	6		20	81.5
133		103	93.7	12.9		32.9	95.6
134		76.7	48	26.8	15.6	36.9	
135		80	60	23.5		41.4	64
136		70.3	38	14.8		32.6	
137		86.3	64.9	45.6		50.7	67.3
138		94.3	67	35			40.4
139		77.6	59.9	9.2		34	81.1
140		88.3	79.2	15.4		37.5	80.4
141		82.6		23.5			37.7
142		99.2	51	21.3		38.3	
143		90	27	8.8			29
144		76.9	59.5	-5.7		14.5	62
145		100.2	82.5	9.1		18.9	84.8

Ex. No.	Structure	I to S_A	to S_C	to S_{M1}	to K	to S_C	to S_A
146		96	74				
147		106.1	95.6	-8.8		9.1	97.8
148		88	61				
149		100.8	90.9	-8.2		13.6	93.4
150		64.80	59.1		19.3	25.1	61.6
151		96.3	68.7	-4.4		25.6	71.7
152		75.2	32.3	-8.7		5.1	34.6
153		67.9	19	-8.4		12.6	
154		96.1	40	-32		8.7	
155		106.1	83.2	-27.4		22.8	85.7
156		102.1	79.2	-27.3		20.9	81.7
157		78.4	55.2	-24.5		2.7	57.6
158		79.00	57.5		-29.8	9.9	
159		55.9	12	-24.5			16.4
160		72.00	47.6		-25	15.7	
161		79.50	62.00	-25.40		-10.40	
162		73.20	55.1		-29	25.4	

Ex. No.	Structure	I to S_A	to S_C	to S_{M1}	to K	to S_C	to S_A
163		94.6	81.6	-16.7		-9.8	84
164		73.9		-22.9			28.9
165		71.8	35.3	-21.6		26.6	39.8
166		91.6	57.6	12.6		20	60.3
167		76.8	4	<-40			20
168		74.7	40	-36.5	22.4	43.7	
169		84.4	56	<-35		-34.7	
170		94.5	62.8	<-47			65.3
171		76.7		<-47			
172		80.2	25	<-47			
173		82	63.5	-44.5		-32	65.8
174		84.3	55.7	<-47		-35.5	58.2
175		83.1		-14.8			36.2
176		70.7	49.1	10.1		14.7	50.5
177		73.8	50.1	-9.6		17	52.1
178		78.3		-40.2			5.7
179		80.3		-35.9			6.4
180		83.1	69.8	<-40		0.7	71.2
181		84.3	57.4	-34.5		6.8	59.8

Ex. No.	Structure	I to S_A	to S_C	to S_{MI}	to K	to S_C	to S_A
182		86.3	73.7	-20.3		-12.6	75.9
183		79.1	58	-23.3		6.6	
184		80.3	55	-24.7		7.8	58.6
185		78	70.4	-33		11.9	72.6
186		77.6	74	0.6	-11.2	3.2	77.3
187		73/71	54.4	8.7		15.6	56.6
188		93.5	84.4	<-47		<-47	86.9
189		61.9	54.4	16.3		21.8	56.5
190		55.2	47.2	8.2	-29.4	22.1	50.1
191		69.2	61.3	-22.2		-8.6	63.9
192		61.6	57	4.2		16.4	
193		32	24	-14		12.5	26.6
194		69.6	63		16.2	17.8	65
195		78.8	51.8	-19		10.5	55
196		50	37.1		<5		
197		56.7	38.6	9.8	2.9	23.8	40.7
198		61.9	54.4	16.3		21.8	56.5
199		85.4	71.1	-0.9		10.1	73.1
200		86.7	78.1	-5		22.7	80.4
201			47.1	-2		13.3	
202		108.9	93.6	-19.9		39.2	

Ex. No.	Structure	I to S_A	to S_C	to S_{M1}	to K	to S_C	to S_A
203		73		-41.9			-31.5
204		99.5	77.8	-14.5		-1.6	80.3
205		129.7	80.4	-5		17.6	82.8
206		82	70.6	-39.5		-30.8	73
207		81	68	<RT			
208		100.8	94.1	-12.7		19.2	96.5
209		78.2	60.3	-11.3		32.5	62.5
210		100.5	79.8	-0.6		11.7	82.3
211		120.1	103.1	-5.3		17.9	105.9
212		100.9	75.5	2.2		24	78
213		111.5	94.2	-7.3		14.4	96.7
214		96.4	85.4	59.2		63.2	87.6
215		82	65	2			
216		68	48	-7			
217		93	81	24			
218		82.5	67.4	4			
219		73.8	57.7	1.7			

The data in Table 1 shows that most of the compounds of the invention exhibit smectic mesophases

and that many of the compounds exhibit a broad smectic C mesophase, which makes the compounds well-suited for use in liquid crystal display devices. As a result of the breadth of the smectic C mesophase, the compounds are useful in admixture with themselves or with other liquid crystal compounds, even at high concentration.

The smectic C layer spacing of selected compounds of the invention was measured as a function of temperature by Small Angle X-ray Scattering (SAXS), essentially as described in U.S. Patent No. 5,417,883, and a plot of the data is shown in Figure 1. This data indicates that the compounds of the invention generally exhibited maintenance or expansion of the smectic C layer spacing with decreasing temperature (and can be used to control layer spacing with respect to temperature as described in U.S. Patent No. 5,417,883). The expansion rate varied with structure.

<u>Examples 220 through 236</u>

A series of devices, each containing a chiral compound of this invention (designated by a parenthetical reference to Example No. in Table 2 below), was prepared essentially as described in U.S. Patent No. 5,377,033 (Radcliffe). The ITO-constituted electrodes of each device were connected to an arbitrary waveform generator with variable output voltage. The device was driven by a voltage waveform consisting of bipolar, square pulses of ±10V/μm amplitude, spaced 30 milliseconds apart by a train of square pulses having the same width and 3.3 V/μm amplitude. The device was heated to the temperatures noted in Table 3 (below) and the polarization (nC/cm^2), the $\tau_{electric}$, the smectic viscosity, and the tilt angle φ_t were determined as described below:

The polarization of the device was determined essentially as described by Miyasato et al. in Jap. J. Appl. Phys. 22, 661 (1983). The electronic response time, $\tau_{electric}$, was derived from the displacement current of the ferroelectric liquid crystal device under an applied square voltage pulse. The current was viewed on a 100 megahertz bandwidth oscilloscope. The usual decaying exponential, associated with a dielectric filled capacitor, was followed by the spontaneous polarization (P_s) switching pulse. The time from the rising edge of the voltage pulse to the peak of the P_s pulse was taken to be $\tau_{electric}$. The rotational viscosity (smectic viscosity, η) was calculated as shown below :

$$\eta(10^{-3}\ kg / m \cdot s) = 0.01 \cdot P_s \cdot E \cdot \tau_{electric},$$

where the units of P_s, E, and $\tau_{electric}$ are respectively nC/cm^2†, V/μm, and μs. The tilt angle φ_t of the mixture was taken to be half the angle separating the extinction points of the driven states. The results given in Table 2 show fast response times over a wide temperature range.

Table 2.

Example No.	Temperature (°C)	Reduced Temperature (T-Tc, °C)	Polarization (nC/cm²)	Response Time (μs)	Smectic Viscosity (mPa · s)	Tilt Angle (degrees)
220 (using compound of Ex. No. 144)	50.2	-9.3	25.3	5.8	14.6	22.6
	39.6	-19.9	31.6	7.0	22.0	24.1
	29.6	-29.9	37.1	8.1	29.9	24.6
	19.5	-40.0	42.2	9.9	41.7	24.7
	14.2	-45.3	45.0	11.2	50.4	24.7

Example No.	Temp r-ature (°C)	Reduced Temper-ature (T-T_C, °C)	Polari-zation (nC/cm^2)	Resp nse Time (μs)	Smectic Viscosity (mPa · s)	Tilt Angle (degrees)
221 (using compound of Ex. No. 40)	40.5	-9.9	27.1	5.0	13.6	20.8
	30.3	-20.1	33.1	6.4	21.2	21.7
	20.1	-30.3	38.8	7.5	29.1	22.1
	9.9	-40.5	45.2	9.4	42.5	0.0
222 (using compound of Ex. No. 106)	53.0	3.0	2.1	8.0	1.7	
	42.7	-7.3	3.7	37.9	14.0	16.1
	32.5	-17.5	3.8	76.5	29.1	18.1
	22.1	-27.9	2.1			18.9
223 (using compound of Ex. No. 45)	73.5	-8.5	27.5	5.2	14.4	23.3
	62.9	-19.1	34.6	6.1	21.0	24.9
	52.7	-29.3	41.2	7.0	28.6	25.6
	42.7	-39.3	47.0	8.2	38.4	25.8
	32.3	-49.7	53.3	10.3	54.8	25.9
	22.3	-59.7	59.3	13.4	79.6	25.7
	12.0	-70.1	61.2	19.5	119.6	25.5
224 (using compound of Ex. No. 46)	87.6	-8.4	26.7	5.5	14.7	28.6
	77.5	-18.5	32.7	6.3	20.5	30.2
	67.2	-28.8	38.0	7.0	26.5	31.8
	57.0	-39.0	42.6	8.0	33.9	32.0
	46.8	-49.2	47.3	9.4	44.7	32.0
	36.5	-59.5	52.4	11.5	60.5	31.7
	26.2	-69.8	57.5	15.4	88.3	31.4
	16.0	-80.1	63.7	21.9	139.5	31.1
225 (using compound of Ex. No. 93)	70.7	-1.3	6.4	6.2	4.0	15.3
	60.3	-11.7	9.7	10.5	10.2	18.0
	50.2	-21.8	11.7	13.1	15.2	18.8
	40.1	-31.9	13.1	16.5	21.6	19.1
	30.0	-42.0	14.2	22.1	31.4	19.1
226 (using	91.6	-12.4	23.7	6.4	15.3	28.7
	78.0	-26.0	31.2	8.1	25.4	31.4

Example No.	Temperature (°C)	Reduced Temperature ($T-T_C$, °C)	Polarization (nC/cm^2)	Response Time (μs)	Smectic Viscosity (mPa · s)	Tilt Angle (degrees)
compound	64.1	-39.9	38.5	10.6	40.9	32.6
of Ex.	50.1	-53.9	47.0	14.8	69.8	33.2
No. 73)	36.1	-67.9	58.1	22.6	131.4	33.6
	22.2	-81.8	72.6	39.9	289.4	33.9
227	85.6	-9.9	17.0	6.6	11.2	26.4
(using	75.8	-19.7	20.5	7.5	15.4	27.9
compound	65.6	-29.9	23.1	8.5	19.5	28.4
of Ex.	55.8	-39.7	25.2	9.7	24.5	28.4
No. 133)	45.6	-49.9	27.9	11.4	31.9	28.3
	35.6	-59.9	30.8	14.0	43.0	28.0
	25.5	-70.0	34.8	18.3	63.7	
228	69.1	-9.9	19.0	7.4	14.1	22.2
(using	58.9	-20.1	22.0	9.7	21.3	23.2
compound	49.0	-30.0	23.9	12.7	30.4	23.3
of Ex.	38.8	-40.2	25.6	17.3	44.3	22.9
No. 204)	29.1	-49.9	27.0	24.8	67.0	22.2
	19.0	-60.0	28.5	42.0	119.7	21.4
	9.1	-69.9	30.1	77.2	232.4	20.6
229	55.3	-10.2	21.4	7.9	16.8	23.5
(using	45.4	-20.1	24.2	9.3	22.5	24.6
compound	35.5	-30.0	27.5	11.7	32.1	24.8
of Ex.	25.2	-40.3	30.0	15.8	47.4	24.7
No. 173)	15.2	-50.3	31.6	23.3	73.8	24.4
	5.4	-60.1	33.8	39.7	134.5	23.9
230	62.1	-10.1	21.7	8.8	19.0	27.4
(using	52.1	-20.1	27.9	10.2	28.3	29.1
compound	42.0	-30.2	34.6	12.1	41.8	29.8
of Ex.	32.1	-40.1	41.4	15.3	63.5	30.0
No. 206)	22.1	-50.1	49.2	20.5	100.9	30.1
	12.1	-60.1	56.2	30.2	169.8	30.0
	2.1	-70.1	65.4	51.8	338.6	29.8

Example No.	Temperature (°C)	Reduced Temperature ($T-T_C$, °C)	Polarization (nC/cm^2)	Response Time (μs)	Smectic Viscosity (mPa · s)	Tilt Angle (degrees)
231 (using compound of Ex. No. 101)	72.1	-4.6	4.4	8.7	3.9	15.2
	67.2	-9.5	5.2	10.3	5.3	16.2
	56.8	-19.9	6.9	11.1	7.7	16.3
	46.8	-29.9	8.1	12.1	9.8	16.1
	36.7	-40.0	9.0	13.8	12.4	15.8
	26.7	-50.0	10.5	16.4	17.2	15.6
	16.6	-60.1	11.4	21.5	24.6	15.2
232 (using compound of Ex. No. 216)	39.4	-9.9	74.3	11.5	85.6	35.3
	29.1	-20.2	89.8	16.4	147.2	37.1
	19.1	-30.2	98.3	25.6	251.5	37.9
	9.1	-40.2	101.3	46.2	467.7	38.3
	-1.0	-50.3	104.9	106.2	1114.0	38.4
233 (using compound of Ex. No. 59)	39.3	-6.5	38.1	5.0	19.2	
	32.2	-13.6	47.5	6.9	33.0	
	24.2	-21.6	58.2	8.7	50.6	
	17.0	-28.8	69.3	10.6	73.7	
	9.6	-36.2	82.2	14.0	115.1	
234 (using compound of Ex. No. 63)	77.0	-11.5	38.2	4.6	17.8	
	66.8	-21.7	46.3	5.2	24.0	27.9
	56.8	-31.7	55.6	6.0	33.3	28.6
	46.9	-41.6	61.1	7.0	42.7	28.8
	36.9	-51.6	68.1	8.7	59.4	28.8
	26.8	-61.7	74.4	11.5	85.2	
	16.7	-71.8	80.1	16.4	131.2	
235 (using compound of Ex. No. 53)	43.1	-7.1	42.7	4.2	17.9	
	38.4	-11.8	49.0	5.1	25.1	
	33.7	-16.5	55.5	6.0	33.6	
	28.7	-21.5	62.8	7.1	44.4	
	23.7	-26.5	70.0	8.3	57.8	
	18.8	-31.4	78.1	9.7	76.0	
	13.6	-36.6	88.4	11.5	101.8	

Example No.	Temperature (°C)	Reduced Temperature (T-Tc, °C)	Polarization (nC/cm²)	Response Time (μs)	Smectic Viscosity (mPa · s)	Tilt Angle (degrees)
236 (using compound of Ex. No. 182)	68.0	-10.0	13.0	7.4	9.6	23.4
	58.0	-20.0	16.2	8.4	13.6	24.7
	48.0	-30.0	17.6	10.0	17.6	25.0
	38.0	-40.0	19.1	12.6	24.1	24.9
	28.0	-50.0	20.4	16.7	34.1	24.6
	18.0	-60.0	21.9	24.0	52.6	24.1
	8.0	-70.0	23.4	39.9	93.4	23.6

Example 237

A device was prepared essentially as described above using a mixture of 90 weight % of the compound of the invention prepared in Example 93 and 10 weight % 5-octyloxy-2-[4-(3-(4-(nonafluorobutoxy)octafluorobutoxy)-2,2,3,3,4,4-hexafluorobutoxy)2-(S)-fluoropropoxyphenyl]pyrimidine (prepared essentially as described in Example 12 of International Patent Publication No. WO 96/33251), and the electrooptical properties of the mixture were measured essentially as previously described. The results are shown in Table 4.

Example 238 - 242

In the following Examples, a series of devices, each containing at least one chiral compound of this invention, were prepared essentially as described in U.S. Patent No. 5,377,033 (Radcliffe) and filled with a mixture of liquid crystal compounds. The composition of each mixture (in weight percent) and the phase transition temperatures of the mixtures are shown in Table 3.

Compound A, 5-hexyl-2-[4-(6-(2-(2-(2-(trifluoromethoxy)tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)hexyl)phenyl]pyrimidine, was prepared essentially as in Example 1 by combining 6-(2-(2-(2-(trifluoromethoxy)tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)hex-1-ene (6.0 g, 12.4 mmol) and 5-hexyl-2-(4-(trifluoromethylsulfonyl)phenyl)pyrimidine (4.70 g, 12.4 mmol). The resulting mixture was quenched with water, and the resulting crude product was isolated by extraction with toluene and further purified essentially as in Example 1, followed by Kugelrohr distillation (187-92°C at 0.01 to 0.015 torr) to provide a yield of 4.45 g.

Compound B, 5-heptyloxy-2-[4-(6-(2-(2-(2-(trifluoromethoxy)tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)hexyl)phenyl]pyrimidine was prepared using essentially the procedure of Example 1 by combining 6-(2-(2-(2-(trifluoromethoxy)tetrafluoroethoxy)tetrafluoroethoxy)-2,2-difluoroethoxy)hex-1-ene and 5-heptyloxy-2-(4-(trifluoromethylsulfonyl)phenyl)pyrimidine.

Compound C, 5-heptyloxy-2-[4-(6-(3-(pentafluoroethoxy)-2,2,3,3-tetrafluoropropoxy)hexyl)phenyl]pyrimidine was prepared using essentially the procedure of Example 1 by combining 3-(pentafluoroethoxy)-2,2,3,3-tetrafluoropropoxy)hex-1-ene and 5-heptyloxy-2-(4-(trifluoromethylsulfonyl)phenyl)pyrimidine.

Table 3.

Compound	Example No.					
	237	238	239	240	241	242
Example 93	90					
Example 12 of	10					

Compound	Example No.					
	237	238	239	240	241	242
WO 96/33251						
Example 155		15	15	10		
Example 63		30	30	20		
Example 211		25				
Example 30 of US 5658491		10	10	10		
Compound A		20	20	20		
Example 204			25			
Example 34				40		
Example 200					54	
Example 13					46	
Example 112						15
Example 44						20
Example 35						20
Example 151						10
Compound B						15
Compound C						20
Transition Temperature Data (°C)						
I to S_A	112.3	106.1	102.6	101.2	96.0	98.0
to S_C	55.4	74.0	68.2	64	79.2	55.4
to S_{M1}	<6	<1	<1	<-1	10	<-5

Table 4.

Example No.	Temperature (°C)	Reduced Temperature (T-T$_C$, °C)	Polarization (nC/cm^2)	Response Time (μs)	Smectic Viscosity (mPa · s)	Tilt Angle (degrees)
237	46.6	-8.8	13.4	6.1	8.2	14.8
	36.7	-18.7	15.7	8.3	13.0	15.5
	26.8	-28.6	17.4	10.9	19.0	15.4
	16.5	-38.9	18.5	15.6	28.8	15.1
	6.4	-49.0	19.8	24.4	48.4	14.8

Example No.	Temperature (°C)	Reduced Temperature (T-Tc, °C)	Polarization (nC/cm²)	Response Time (μs)	Smectic Viscosity (mPa · s)	Tilt Angle (degrees)
238	62	-10	22.5	6.1	13.7	23.3
	52	-20	27.7	7.3	20.2	24.9
	42	-30	31.9	9.0	28.7	25.6
	32	-40	36.2	11.4	41.1	25.9
	22	-50	40.7	15.9	64.5	26.0
239	58	-10	20.7	6.3	13.1	22.4
	48	-20	25.4	7.7	19.6	24.0
	38	-30	29.1	9.5	27.5	24.6
	28	-40	32.6	12.1	39.4	24.8
	18	-50	35.7	17.7	63.1	24.8
240	52	-10	24.3	6.3	15.4	
	42	-20	28.8	7.4	21.5	
	32	-30	33.4	9.4	31.4	
	22	-40	37.1	12.8	47.5	
	12	-50	41.8	18.7	78.2	
241	69	-10	33.7	6.9	23.1	29.0
	59	-20	41.7	8.0	33.3	30.9
	49	-30	48.5	9.6	46.6	31.8
	39	-40	57.0	12.0	68.3	32.3
	29	-50	64.9	15.7	102.2	32.5
	19	-60	76.3	22.2	169.2	32.7
242	49	-7	16.4	5.6	9.2	17.7
	38	-17	21.6	8.5	18.3	19.6
	28	-27	26.3	11.1	29.3	20.6
	23	-32	28.4	12.9	36.6	20.9
	18	-37	31.1	15.3	47.8	21.1
	8	-47	36.8	23.4	86.0	21.5

The results shown in Table 4 indicate that the compounds of the invention can be used in mixtures in liquid crystal display devices to provide low mixture viscosities and improve the performance of the devices.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

<u>What Is Claimed Is:</u>

1. Fluorine-containing, chiral liquid crystal compounds having smectic mesophases or latent smectic mesophases, the compounds comprising (a) a chiral fluorochemical terminal portion comprising (i) at least one chiral center, which can optionally be heteroatom-substituted; (ii) a terminal fluoroalkyl, fluoroether, perfluoroalkyl, or perfluoroether group; and (iii) an alkylene or fluoroalkylene group optionally containing at least one catenary ether oxygen atom; (b) a chiral or achiral terminal portion consisting of a hydrocarbon or hydrocarbon ether group and, when chiral, comprising at least one chiral center, which can optionally be heteroatom-substituted; and (c) a central core connecting said terminal portions; said alkylene or fluoroalkylene group of said chiral fluorochemical terminal portion having at least 3 in-chain atoms and being located between said chiral center of said chiral fluorochemical terminal portion and said central core.

2. The compounds of Claim 1 wherein said chiral fluorochemical terminal portion is represented by the formula $-D-R^*-D-R_f$, where R^* is a cyclic or acyclic chiral moiety containing at least one chiral center; R_f is fluoroalkyl, perfluoroalkyl, fluoroether, or perfluoroether; and each D is independently and non-directionally selected from the group consisting of a covalent bond,

$-C(=O)-O-C_rH_{2r}-$, $-O-C_rH_{2r}-$, $-O-(O=)C-C_rH_{2r}-$, $-C\equiv C-$, $-CH=CH-$, $-C(=O)-$,

$-O(C_sH_{2s}O)_tC_{r'}H_{2r'}-$, $-C_rH_{2r}-$, $(C_sH_{2s}O)_tC_{r'}H_{2r'}-$, $-O-$, $-S-$,

$-OSO_2-$, $-SO_2-$, $-SO_2-C_rH_{2r}-$, $-C_rH_{2r}-\underset{\displaystyle C_pH_{2p+1}}{\underset{|}{N}}-SO_2-$, $-N(C_pH_{2p+1})-$,

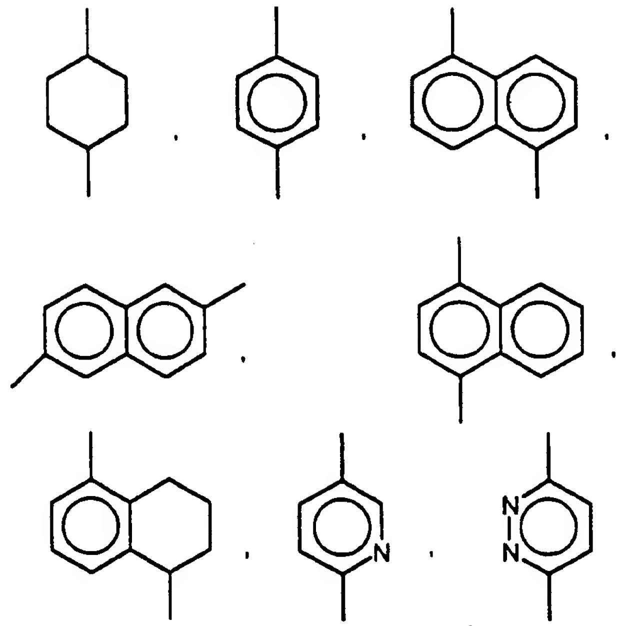
$-C_rH_{2r}-N-C(=O)-$, $-CH=N-$,

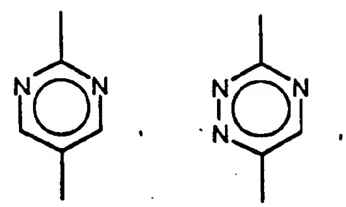
and combinations thereof, where one or more hydrogen atoms can optionally be replaced with fluorine, and where r and r' are independently integers of 0 to about 20, s is independently an integer of 1 to about 10 for each $(C_sH_{2s}O)$, t is an integer of 1 to about 6, and p is an integer of 0 to about 4; with the proviso that there are at least 3 in-chain atoms between said central core and at least one said chiral center of R*.

3. The compounds of Claim 1 wherein said compounds are represented by the general formula (I):

$$R-\underset{\displaystyle X_l}{\underset{|}{(M)}}{}_a-A\underset{\displaystyle Y_m}{\underset{|}{(N)}}{}_bB\underset{\displaystyle Z_n}{\underset{|}{(P)}}{}_c-D-R^*-D-R_f \qquad (I)$$

where M, N, and P are each independently selected from the group consisting of





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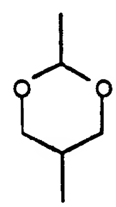
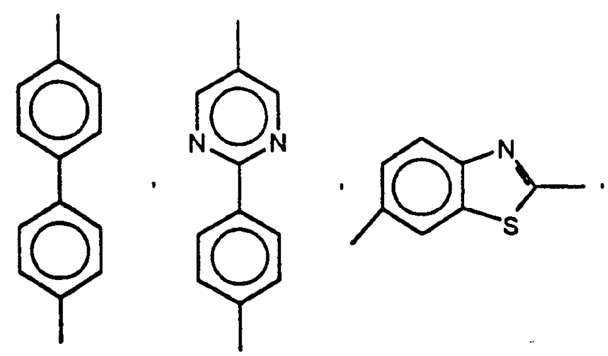
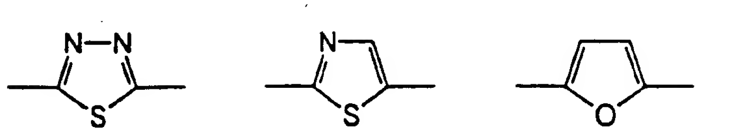
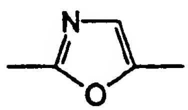
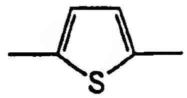
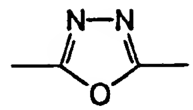
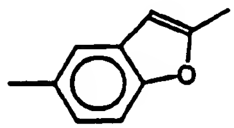






 ,  ,  , and



a, b, and c are each independently zero or an integer of from 1 to 3, with the proviso that the sum of a + b + c be at least 1;

each A and B are non-directionally and independently selected from the group consisting of a covalent bond,

-C(=O)-O-, -C(=O)-S-, -C(=O)-Se-,

-C(=O)-Te-, $-(CH_2CH_2)_k-$ where k is 1 to 4, -CH=CH-, -C≡C-, -CH=N-, $-CH_2-O-$, -C(=O)-, and -O- ;

each X, Y, and Z are independently selected from the group consisting of -H, -Cl, -F, -Br, -I, -OH, $-OCH_3$, $-CH_3$, $-CF_3$, $-OCF_3$, -CN, and $-NO_2$;

each l, m, and n are independently zero or an integer of 1 to 4;

each D is non-directionally and independently selected from the group consisting of a covalent bond, $-C(=O)-O-C_rH_{2r}-$, $-O-C_rH_{2r}-$, $-O-(O=)C-C_rH_{2r}-$, -C≡C-, -CH=CH-, -C(=O)-,

$-O(C_sH_{2s}O)_tC_{r'}H_{2r'}-$, $-C_rH_{2r}-$, $(C_sH_{2s}O)_tC_{r'}H_{2r'}-$, -O-, -S-,

$-OSO_2-$, $-SO_2-$, $-SO_2-C_rH_{2r}-$, $-C_rH_{2r}-\underset{\displaystyle C_pH_{2p+1}}{\underset{|}{N}}-SO_2-$, $-N(C_pH_{2p+1})-$,

$-C_rH_{2r}-\underset{\displaystyle C_pH_{2p+1}}{\underset{|}{N}}-C(=O)-$, $-CH=N-$, and combinations thereof,

where one or more hydrogen atoms can optionally be replaced with fluorine, and where r and r' are independently integers of 0 to about 20, s is independently an integer of 1 to about 10 for each $(C_sH_{2s}O)$, t is an integer of 1 to about 6, and p is an integer of 0 to about 4;

R is selected from the group consisting of
$-O-((C_{q'}H_{2q'-v'}-(R')_{v'})-O)_w-C_qH_{2q+1-v}-(R')_v$,
$-((C_{q'}H_{2q'-v'}-(R')_{v'})-O)_w-C_qH_{2q+1-v}-(R')_v$,

$-C(=O)-O-C_qH_{2q+1-v}-(R')_v$, $-O-(O=)C-C_qH_{2q+1-v}-(R')_v$,

```
     D
    / \
 —W   W—CqH2q+1-v—(R')v , and
    \ /
     D
```

$-CR'H-(D)_g-CR'H-C_qH_{2q+1-v}-(R')_v$,

where each R' is independently selected from the group consisting of $-Cl$, $-F$, $-CF_3$, $-NO_2$, $-CN$, $-H$, $-C_qH_{2q+1}$,

$-O-(O=)C-C_qH_{2q+1}$, $-C(=O)-O-C_qH_{2q+1}$, $-Br$, $-OH$, and $-OC_qH_{2q+1}$; q' is independently an integer of 1 to about 20 for each $(C_{q'}H_{2q'}-O)$; q is an integer of 1 to about 20; w is an integer of 0 to about 10; v is an integer of 0 to about 2; each v' is independently an integer of 0 to

about 2; g is an integer of 1 to about 3; each D is independently and non-directionally selected from the group set forth for D above, with the proviso that the ring containing D has from about 3 to about 10 ring atoms; each W is independently selected from the group consisting of N, CR′, and SiR′; and R can be chiral or achiral; and

R* is a cyclic or acyclic chiral moiety containing at least one chiral center; and

R_f is fluoroalkyl, perfluoroalkyl, fluoroether, or perfluoroether;

with the proviso that there are at least 3 in-chain atoms between said central core structure $-(M)_a-A-(N)_b-B-(P)_c-$ and at least one said chiral center of R*.

4. The compounds of Claim 3 wherein said R* is selected from the group consisting of
$-O-((C_{q'}H_{2q'-v'}-(R')_{v'})-O)_w-C_qH_{2q-v}-(R')_v-$,
$-((C_{q'}H_{2q'-v'}-(R')_{v'})-O)_w-C_qH_{2q-v}-(R')_v-$,
$-C(=O)-O-C_qH_{2q-v}-(R')_v-$, $-O-(O=)C-C_qH_{2q-v}-(R')_v-$,

```
      D
     / \
 —W     W—, and -CR'H-(D)g-CR'H- ,
     \ /
      D
```

where each R' is independently selected from the group consisting of -Cl, -F, $-CF_3$, $-NO_2$, -CN, -H, $-C_qH_{2q+1}$, $-O-(O=)C-C_qH_{2q+1}$, $-C(=O)-O-C_qH_{2q+1}$, -Br, -OH, and $-OC_qH_{2q+1}$; q' is independently an integer of 1 to about 20 for

each $(C_{q'}H_{2q'}-O)$; q is an integer of 1 to about 20; w is an integer of 0 to about 10; v is an integer of 0 to about 3; each v' is independently an integer of 0 to about 3; g is an integer of 1 to about 3; each D is independently and non-directionally selected from the group set forth for D in Claim 3, with the proviso that the ring containing D has from about 3 to about 10 ring atoms; each W is independently selected from the group consisting of N, CR', and SiR'; and with the proviso that R* is chiral.

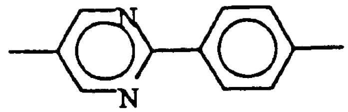
5. The compounds of Claim 3 wherein said compounds are represented by the general formula (II):

$$R''-(O)_j-G-D'-R^*-(C_{s'}H_{2s'}O)_{t'}C_{r''}H_{2r''}-R_f \qquad (II)$$

where R'' is $(R')_v-C_qH_{2q+1-v}$, where q is an integer of 2 to about 10, each R' is independently selected from the group consisting of hydrogen, fluorine, chlorine, methyl, and perfluoromethyl, and v is an integer of 1 to about 2;

j is an integer of 0 or 1;

G is selected from the group consisting of



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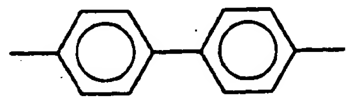

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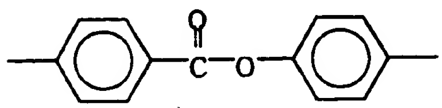
, and



,

where one or more aromatic hydrogen atoms can be replaced with fluorine;

D′ is selected from the group consisting of $-O\text{-}(C_sH_{2s}O)_t\text{-}C_{r'}H_{2r'}-$, $-C_rH_{2r}-$, $-(C_sH_{2s}O)_t\text{-}C_{r'}H_{2r'}-$, and $-O-C_rH_{2r}-$, where r and r' are independently integers of 0 to about 12, s is independently an integer of 1 to about 10 for each $(C_sH_{2s}O)$, and t is an integer of 1 to about 3;

R* is selected from the group consisting of $-C_qH_{2q-v}-(R')_v-$ and

```
      D″
     / \
 —W     W—,
     \ /
      D″
```

where R′ is -F, q is an integer of 1 to about 4, v is an integer of 1 to about 3, W is N or CH, and D″ is -C(=O)-O- or $-CH_2-$;

s′ is an integer of 1 to about 6;

t′ is an integer of 0 or 1;

r″ is an integer of 1 to about 3; and

R_f is selected from the group consisting of $-C_qF_{2q+1}$ and $-(C_xF_{2x}O)_zC_yF_{2y+1}$, where q is an integer of 1 to about 6, x is independently an integer of 1 to about 10 for each $(C_xF_{2x}O)$, y is an integer of 1 to about 8, and z is an integer of 1 to about 5;

with the proviso that there are at least 3 in-chain atoms between said central core structure G and at least one said chiral center of R*.

6. Fluorine-containing, chiral liquid crystal compounds having smectic mesophases or latent smectic mesophases, the compounds comprising (a) a chiral fluorochemical terminal portion comprising (i) at least one chiral center, which can optionally be heteroatom-substituted; (ii) a terminal perfluoroether group; and (iii) an alkylene group optionally containing at least one catenary ether oxygen atom; (b) a chiral or achiral terminal portion consisting of a hydrocarbon or hydrocarbon ether group, and, when chiral, comprising at least one chiral center, which can optionally be heteroatom-substituted; and (c) a central core connecting said terminal portions; said alkylene group of said chiral fluorochemical terminal portion having at least 3 in-chain atoms and being located between said chiral center of said chiral fluorochemical terminal portion and said central core.

7. Fluorine-containing, chiral liquid crystal compounds having smectic mesophases or latent smectic mesophases, the compounds comprising two fluorochemical terminal portions and being represented by the general formula VIII:

$$R_f-CH_2O-C_{n'}H_{2n'}-(O)_j-\underset{X_l}{(M)_a}-A\underset{Y_m}{(N)_b}B\underset{Z_n}{(P)_c}-D-R^*-D-R_f \qquad \text{(VIII)}$$

where n' is an integer of 0 to about 10; j is an integer of 0 or 1; each R_f moiety is independently selected from the group consisting of fluoroalkyl, fluoroether, perfluoroalkyl, and perfluoroether; and all other moieties are as defined in Claim 3 above.

8. Chiral liquid crystal intermediate compounds represented by the following general formulas IV, VI, and VII:

$$B''\underset{Z_n}{(P)_c}-D-R^*-D-R_f \qquad \text{(IV)},$$

and

$$A''\underset{Y_m}{(N)_b}B\underset{Z_n}{(P)_c}-D-R^*-D-R_f \qquad \text{(VI)},$$

where N, P, b, c, B, Y, Z, m, n, D, R*, and R_f are as defined in Claim 4; and A'' and B'' are selected from the group consisting of -H, -Cl, -Br, -I, -OH, -COOH, $-CH(CH_2OH)_2$, -SH, -SeH, -TeH, $-NH_2$, -COCl, -CHO, $-C\equiv CH$, dialkyl borane, $-CH=CH_2$, $-OSO_2R_f'''$, $-OSO_2CH_3$, $-OSO_2-cyclo(C_6H_4)-CH_3$, $-CH_2COOH$,

$-NH(C{=}O)OC_qH_{2q+1}$, -NCO, and $-CH(C(O)O-C_qH_{2q+1})_2$, where R_f''' is a perfluoroalkyl group having from 1 to about 10 carbon atoms and q is an integer of 0 to about 20.

9. The compounds of any of Claims 1, 2, 3, 4, 7, or 8 wherein said R_f is perfluoroalkyl or perfluoroether.

10. The compounds of any of Claims 1, 2, 3, 4, 7, or 8 wherein said R_f is perfluoroether.

11. A mixture of liquid crystal compounds comprising at least one fluorine-containing liquid crystal compound of any of Claims 1, 2, 3, 4, 5, 6, 7, 9, or 10.

12. A liquid crystal display device containing at least one fluorine-containing liquid crystal compound of any of Claims 1, 2, 3, 4, 5, 6, 7, 9, or 10.

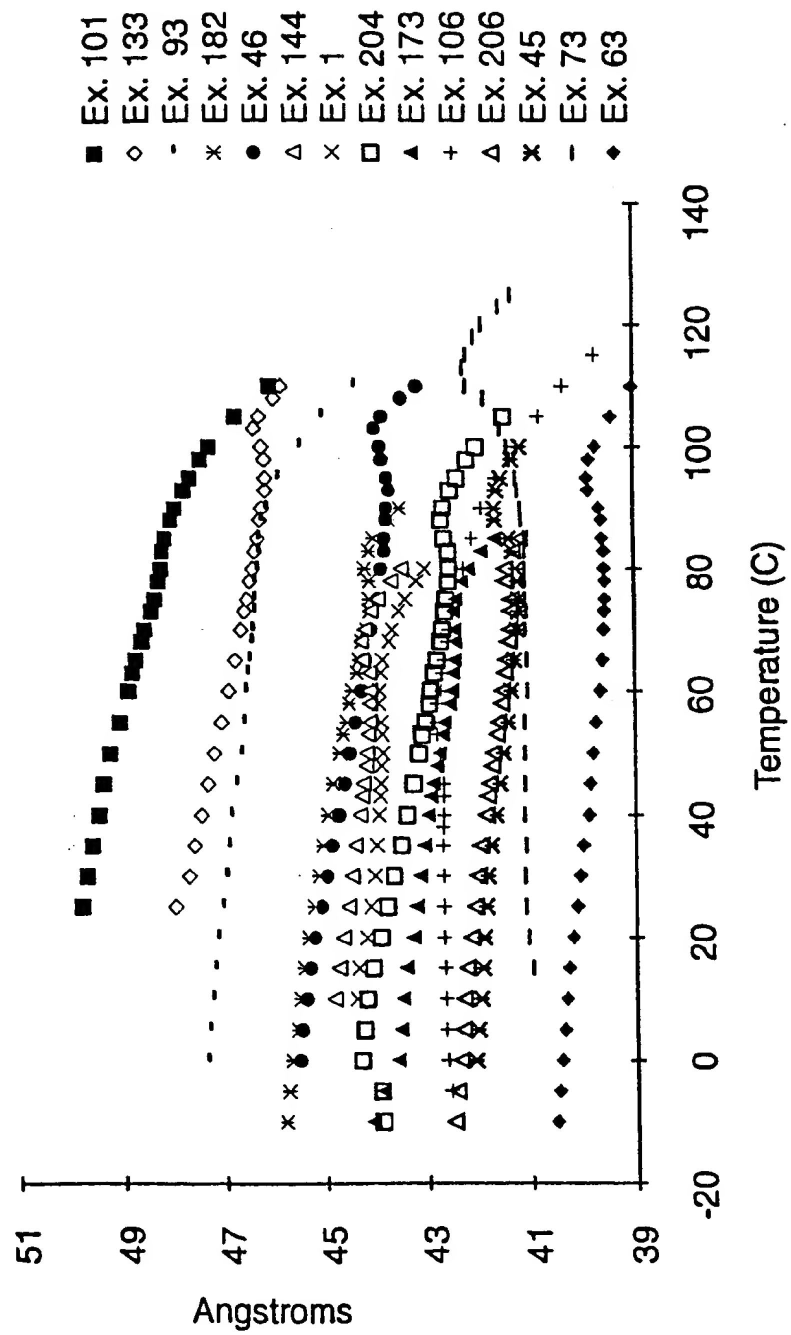

Angstroms
51
49
47
45
43
41
39
Temperature (C)
-20
0
20
40
60
80
100
120
140
Ex. 101
Ex. 133
Ex. 93
Ex. 182
Ex. 46
Ex. 144
Ex. 1
Ex. 204
Ex. 173
Ex. 106
Ex. 206
Ex. 45
Ex. 73
Ex. 63

Fig.1

INTERNATIONAL SEARCH REPORT

Int .tional Application No
PCT/US 98/14624

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D239/26 C09K19/34

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D C09K

Documentation searched other than minimumdocumentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 667 384 A (SUMITOMO CHEMICAL CO) 16 August 1995 see claims 1,11,12; examples 22,28,34,55 ----	1-3,5,9, 11,12
Y	WO 96 33251 A (MINNESOTA MINING & MFG) 24 October 1996 cited in the application see the whole document ----	1-12
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publicationdate of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of theinternational search	Date of mailing of the international search report
8 October 1998	22. 10. 1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Puetz, C

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	NAGASHIMA Y ET AL: "THE SYNTHESIS AND MESOMORPHIC PROPERTIES OF FERROELECTRIC LIQUID CRYSTALS WITH A FLUORINATED ASYMMETRIC FRAME" LIQUID CRYSTALS, vol. 23, no. 4, October 1997, pages 537-546, XP000723914 see page 540, line 1 - page 541, left-hand column see tables 1,2 see scheme 1	1-12
A	EP 0 499 221 A (CANON KK) 19 August 1992 see page 7, line 1 - page 22, line 46 see examples	1,11,12
A	EP 0 434 297 A (SUMITOMO CHEMICAL CO) 26 June 1991 see claims 1-4	1
A	EP 0 301 511 A (CANON KK) 1 February 1989 see page 10, line 10 - page 22, line 7	1,11

1

International application No.
PCT/US 98/14624

INTERNATIONAL SEARCH REPORT

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [X] Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

The ISA considers that the claims 1-12 fail to comply with the prescribed requirements of Article 6 PCT, namely that of support in the description , to such an extent that a meaningful search could not be carried out to cover the claimed subject-matter (cf. Article 17(2)(a)(ii) & (b) PCT). Said noncompliance with Article 6 PCT is considered to arise, due to the scope of said claims encompassing a vast number of possible solutions (compounds), whose number and scope is far greater than that which might reasonably be considered commensurate with the support provided by the examples - it includes a vast number of compounds structurally quite different and thus removed from the structure of said examples, even when taking into consideration a limited generalised structure o the latter. Consequently, the search has been directed to those parts (i.e. compounds) of the claims with are supported by specific examples in the description and/or by a generic structure derived from a limited generalisation thereof commensurate with the scope of of said specific examples (cf. Article 17(2)(b) PCT).

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 98/14624

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0667384 A	16-08-1995	JP 7267885 A	17-10-1995
		US 5779934 A	14-07-1998
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